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STUDIES ON ASPHALTENE CONVERSION AND CATALYST REGENERATION IN TWO-STAGE LIQUEFACTION OF NOVA SCOTIA COALS

FINAL REPORT

by

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EXECUTIVE SUMMARY

This report presents the results of studies on asphaltene conversion and catalyst regeneration in two-stage liquefaction of Nova Scotia coals. Laboratory experiments were carried out to screen potential asphaltene conversion catalysts and determine the degree to which the activity of aged coal liquefaction catalyst can be restored via controlled oxidation. In addition, two-stage coal liquefaction tests were conducted to assess the performance of Shell 317 nickel-molybdenum bimodal catalyst.

A total of nine multi-functional catalysts designed for hydroprocessing heavy feeds were evaluated in the asphaltene conversion study. Alumina support nickel-molybdenum, cobalt-molybdenum and nickel-tungsten type catalysts were tested. The catalysts varied in shape, size, surface area, pore volume and modal pore size distribution. Catalyst screening tests were conducted in a batch reactor system using coal liquid rich in asphaltenes as feed. Activity data were developed for pentane insolubles conversion (PIC), hydrogen content boost (HCB), hydrodenitrogenation (HDN) and hydrodesulphurization (HDS). Shell 317 was found to be superior to the other catalysts in all four activities.

Four aged Amocat 1C catalyst samples and one aged Katalco 550 sample were studied in the catalyst regeneration experiments. Chemical analyses performed on fresh, used and regenerated samples showed substantial carbonaceous deposits, typically 12 - 14%, on the used catalysts. Accumulations of iron, titanium and calcium on the aged samples were quite low. Surface characterizations revealed that the used catalysts had lower pore volumes and surface areas than fresh catalyst. Batch testing showed activity losses in the aged samples ranging from 40 - 100% for PIC, HCB and HDN functionalities. Regeneration via controlled carbon burnoff restored the activities to levels ranging from 70 to 100% of the original.

The two-stage thermal/catalytic coal liquefaction experiments with Shell 317 were done in a once-through processing mode using a continuous-flow bench unit. A total of ten runs were completed with three Sydney area coals and Illinois No. 6, a benchmark American coal. Tests with Donkin Harbour seam coal showed that increasing the catalytic reactor temperature from 410 to 425°C had a positive effect on oil yield. In experiments at similar operating conditions, oil yields from Lingan Harbour, Prince Hub and Donkin Harbour coals were 50, 54 and 55% respectively compared with 58% from Illinois No. 6. The overall performance of Shell 317 was found to be quite similar to that of Amocat 1C, a nickel-molybdenum bimodal catalyst tested previously.

The results of this work indicate that there is still a need for basic research to develop better asphaltene conversion catalyst. The promising results achieved in the catalyst regeneration study suggest that this approach be pursued on a larger scale. It is recommended that collaborative research on catalyst development be initiated and work on catalyst regeneration be continued. The use of a more active catalyst, in particular one with a longer service life, would enhance the overall coal liquefaction process and lower the cost of coal-derived liquids.

INTRODUCTION

Nova Scotia is highly dependent on imported crude oil as a source of transportation and domestic heating fuels. On the other hand, Nova Scotia has abundant coal reserves available for conversion to synthetic liquid fuels. Direct liquefaction is a proven technology for producing liquid hydrocarbons from coal but the coal-derived liquids are not cost competitive with petroleum products at today's prices. In recent years, however, technology advances have been made that significantly improve the economics of direct coal liquefaction.

It is recognized that the development of a commercial synfuels project is an extremely complex task that will cost in the order of hundreds of miliions of dollars if research, pilot plants and demonstration plants are included. However, a commercial coal liquefaction plant in Nova Scotia would strengthen the provincial economy and provide a new market for Cape Breton coal.

The concept of liquefying coal by reacting it with hydrogen at high pressures and temperatures can be traced back to Germany in the early 1900's. Modern day liquefaction operates at substantially lower pressures than the early German technology. The reduction in operating pressure is primarily attributed to the use of better catalysts. In the 1970's and early 80's a number of single-stage direct liquefaction processes, including Exxon Donor Solvent, H-Coal and Ruhrkohle/Veba were developed and tested in large scale pilot plants. Conventional single-stage liquefaction utilizes a single reactor to convert coal into a liquid.

A variation of the so-called conventional direct liquefaction approach appeared in the early 80's. The new concept uses two separate reaction zones instead of one. In this approach coal is dissolved in the first-stage and coal liquid is subsequently upgraded in the second. The use of two separate reaction zones permits the operating conditions for coal dissolution and liquid upgrading to be independently optimized for maximum efficiency and control of product distribution and quality.

Process studies relating to the direct liquefaction of Nova Scotia high volatile bituminous coals were initiated at the Nova Scotia Research Foundation Corporation (NSRFC) in 1978. Initially efforts were concentrated on a low-severity extractive coking process (1 - 3). From 1980-84, experimental work was conducted on medium to high pressure donor solvent extraction (4, 5) and single-stage catalytic hydrogenation (6). Since 1985 efforts have been focused on two-stage liquefaction investigating both thermal/catalytic and catalytic/catalytic process configurations (7 - 12).

The catalyst plays a key role in two-stage coal liquefaction. It is used to increase the hydrogen to carbon ratio of the products, increase distillate production and lower the heteroatom (S, N, O) contents of the products. Hence catalyst activity, selectivity and longevity can have a significant impact on the economics of the overall process.

It is well established that catalysts used for hydroprocessing synthetic fossil fuel feedstocks experience a loss of activity and selectivity with time. The main causes of catalyst deactivation during coal liquefaction are the coverage of active sites, pore mouth

blockage and changes in catalyst structure. Coverage of active sites and pore mouth blockage occur due to rapid buildup of carbonaceous deposits and the accumulation of contaminant metals. Changes in catalyst structure due to sintering are usually caused by prolonged exposure to high temperature.

In our experimental studies with the Cape Breton coals and Illinois No. 6, it is evident that oil yield and product quality vary as a function of coal feedstock. The variation in product distribution is primarily attributed to coal rank. The Sydney area coals are higher rank bituminous than Illinois No. 6 and they yield more heavy asphaltenic materials. Furthermore, they cause more rapid catalyst fouling than Illinois No. 6.

Recently, a research project on asphaltene conversion and catalyst regeneration in two-stage liquefaction of Nova Scotia coals was completed. The project consisted of three main components. Firstly, screening tests were conducted in a batch reactor system to evaluate the capacity of several hydroprocessing catalysts to convert coal-derived asphaltenes into oil. Secondly, laboratory experiments were carried out to determine the degree to which the activity of aged coal liquefaction catalyst can be restored via controlled oxidation. Lastly, a series of two-stage thermal/catalytic bench runs were conducted using Shell 317 nickel-molybdenum bimodal catalyst. The results of this work are presented herein.

TASK 1 - ASPHALTENE CONVERSION STUDY

The conversion of coal to liquid fuels via two-stage direct liquefaction results in the formation of distillate oils, asphaltenes, preasphaltenes and gases. In this technology, product yields and qualities are strongly influenced by the rank of the feed coal and catalyst performance.

Two-stage liquefaction test work at NSRFC has shown that bituminous coals from the Sydney coalfield yield less oil but more asphaltenes and preasphaltenes than Illinois No. 6, an American bituminous coal of lower rank. However, improved hydroprocessing of these asphaltenic components is expected to enhance oil yield.

Since the conversion of asphaltenes into oil involves predominantly catalytic reactions, the use of a superior catalyst would lead to process and product cost improvements. Hence, a screening study was undertaken to identify a superior asphaltene conversion catalyst.

1.1 Properties of Catalysts and Feeds

The selection of candidate materials for the screening study was based on information gathered from commercial catalyst vendors and users in North America. A total of nine multi-functional catalysts designed for hydroprocessing heavy feeds were selected. The physical and chemical properties of the selected materials are summarized in Table 1.

Four conventional nickel-molybdenum type catalysts (Amocat 1C, Katalco 596, Kat-5000 and Shell 317), one cobalt-molybdenum type (Amocat 1A) and one nickel-tungsten type (Katalco 550S) were included in the study. Two additional nickel-molybdenum type catalysts, one containing phosphorus as a modifier (Shell 324) and another with Tio_2 added (HPC 312) were also investigated. The above mentioned catalysts are alumina supported formulations. Loadings of active metals vary over a moderate range. The alumina supports vary in shape, size, surface area, pore volume and modal pore size distribution. At present, the identity and the properties of Cat-X are considered to be confidential information.

Recycle liquids from NSRFC's coal liquefaction test facility were employed as feeds in this study. The properties of the feeds are presented in Table 2. The liquid designated NSRFC-A was produced near the end of a 250-hour two-stage liquefaction operation (RCL-8000) with Prince Hub seam coal. The liquid designated NSRFC-B was generated near the end of a 450-hour two-stage liquefaction run (RCL-9200) with Donkin Harbour seam coal. The pentane insolubles content of NSRFC-B is substantially lower than that of NSRFC-A because solvent deasphalting was applied to the recycle liquid stream throughout RCL-9200.

The asphaltene-rich recycle liquid, NSRFC-A, was used as the principal feed in Tasks 1 and 2. It contained 26.43% pentane insolubles, 7.24% hydrogen, 0.84% nitrogen and 0.120% sulphur.

TABLE 1

CHEMICAL AND PHYSICAL PROPERTIES OF CATALYSTS TESTED

	AMOCAT 1A	AMOCAT 1C	HPC 312	KATALCO 550S	KATALCO 596	KAT-5000	SHELL 317	SHELL 324	CAT-X
MoO_3, Wt. %	15.0	16.0	11.1	-	27.0	14.0	17.9	19.3	-
NiO, Wt. %	-	3.0	3.5	5.0	6.7	3.5	3.3	3.4	-
CoO, Wt. %	3.0	-	-	-	-	-	-	-	-
WO_3, Wt. %	-	-	-	20.0	-	-	-	-	-
P_2O_5, Wt. %	-	-	-	-	-	-	-	5.7	-
TiO_2, Wt. %	-	-	8.0	-	-	-	-	-	-
Size, cm	0.16	0.16	0.13	0.16	0.16	0.08	0.13	0.16	-
Surface Area, M^2/g	165	190	223	200	220	300	230	180	-
Pore Volume, cc/g	0.62	0.85	0.67	0.58	0.39	0.90	0.78	0.43	-
Density, g/cc	0.55	0.61	0.62	0.60	0.92	0.51	0.58	0.78	-
Modal Pore Diameter, A°	100/1500	100/1500	144	100	100	100	100/4-5000	115	-
Shape[a]	E	E	K	S	T/L	E	T/L	E	-

[a] E - Extrudate
K - Cloverlead (4-Lobed)
S - Sphere
T/L - Trilobe

TABLE 2

CHARACTERISTICS OF COAL LIQUID FEEDSTOCKS

	RECYCLE LIQUID NSRFC-A	RECYCLE LIQUID NSRFC-B
Specific Gravity, 60/60°F	1.1034	1.0392
Carbon, Wt. %	90.58	90.04
Hydrogen, Wt. %	7.24	8.96
Nitrogen, Wt. %	0.84	0.56
Sulphur, Wt. %	0.120	0.040
Pentane Insolubles, Wt. %	26.43	7.56

1.2 Experimental Procedures

The selected catalysts were sulphided before being run in the screening test. The sulphiding was carried out in a downflow tubular reactor system. A schematic diagram of the system is shown in Figure 1.

Catalyst sulphiding was accomplished using a 10 mol % mixture of hydrogen sulphide in hydrogen. The procedure was initiated by charging approximately 30 g of dry catalyst to the tubular reactor. Then with the sulphiding gas mixture flowing, the temperature of the reactor was raised to 400°C stepwise in increments of 100°C per hour. The sulphiding operation was continued for 8 hours at 400°C. At the end of this period the reactor was cooled while purging with inert gas to remove adsorbed hydrogen sulphide. The sulphided catalysts were stored in sealed containers until used.

Catalyst activity experiments were conducted in a high pressure batch reactor system. A schematic diagram of the system is presented in Figure 2. The reaction vessel is a 300 cc static basket Robinson-Mahoney style reactor. It is designed for gas/vapour or liquid phase heterogenous reactions. A wire basket is used to contain catalyst in extrudate or bead form. An impeller rotating at high speed maintains liquid flow through the catalyst basket.

All nine catalysts were subjected to an activity screening test with NSRFC-A recycle liquid. The reaction conditions for the screening test were as follows:

Temperature, °C	425
Pressure, MPa	20.68
Time, min	60
Feed Charge, g	105
Catalyst Charge, g	5
Agitator Speed, rpm	800

Additional asphaltene conversion experiments were conducted with two of the nine catalysts. These tests were focused on catalyst performance varying residence time, reaction temperature and liquid feedstock.

A typical batch hydroprocessing experiment was initiated by charging presulphided catalyst and feed liquid to the reactor. Sufficient hydrogen was added to the vessel at room temperature to give the desired pressure at operating temperature. The total heat-up time required to reach 425°C was about 60 minutes, however, only about 10 minutes were required within the zone above 370°C. Hydrogen was added to the vessel during the reaction period to maintain the operating pressure. At the end of the reaction period the vessel was air cooled down to 30°C. At this point the reactor was depressurized and the liquid product was recovered.

The performance of the catalysts was determined by their ability to convert asphaltenic components into pentane soluble products, their ability to raise the hydrogen content of the feed and their heteroatom removal activity (both hydrodenitrogenation and

hydrodesulphurization). The conversion of asphaltenic components was determined from pentane solubilities of the feed and product. By using this approach, conversion of asphaltenes plus preasphaltenes is actually obtained. The hydrogenation and heteroatom removal activities were determined from standard ultimate analyses of the feed and product liquids.

Figure 1 - SCHEMATIC DIAGRAM OF CATALYST REGENERATION APPARATUS

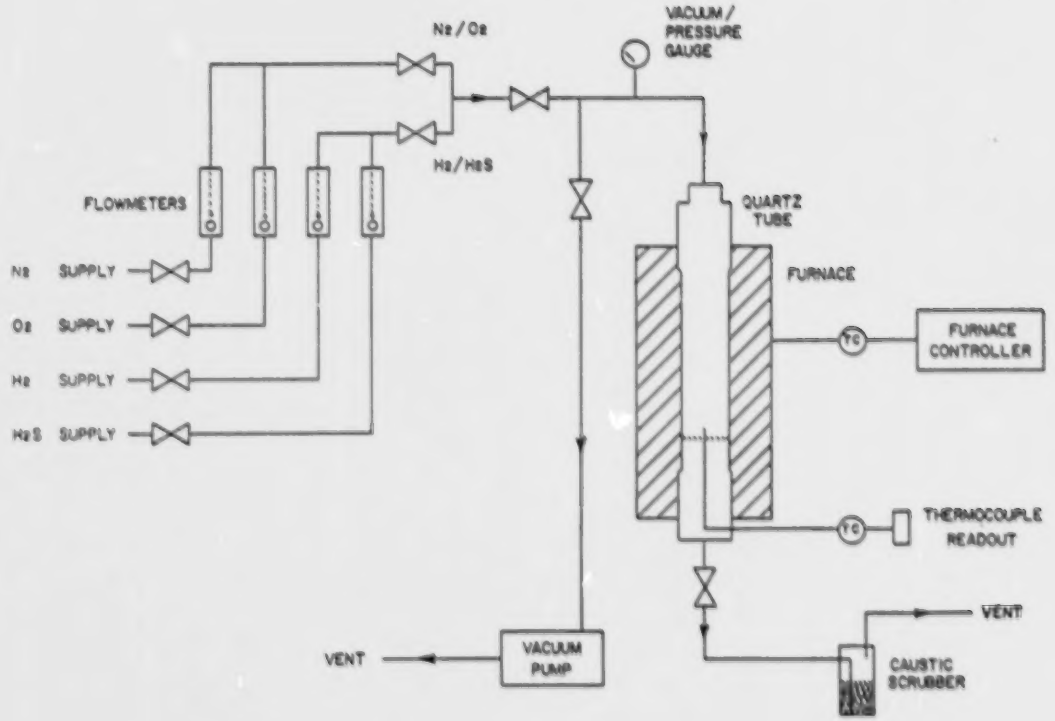
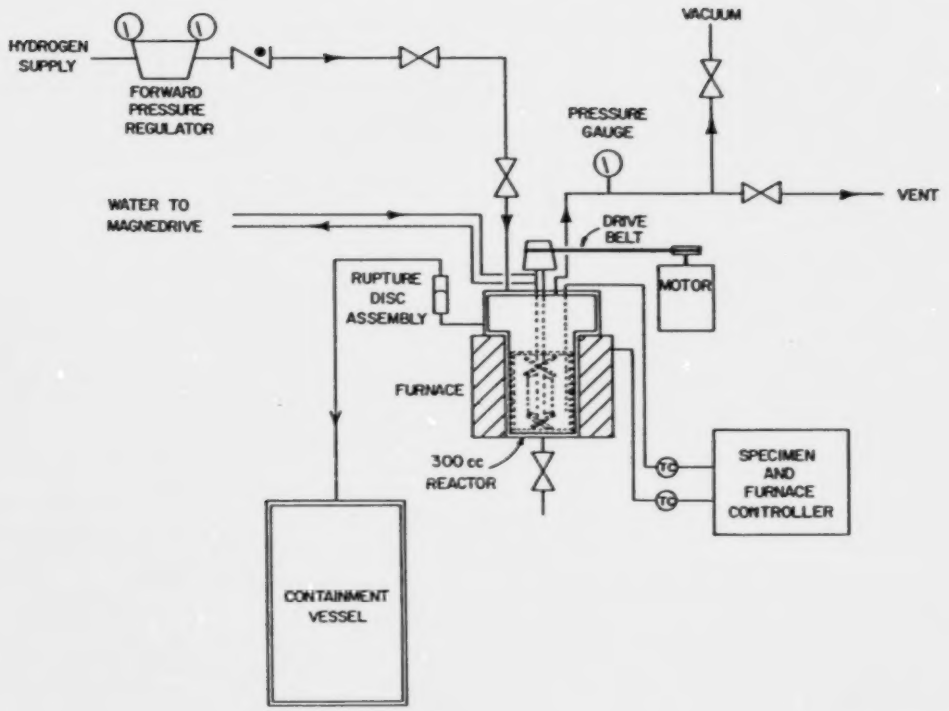


Figure 2 - SCHEMATIC DIAGRAM OF BATCH CATALYTIC REACTOR SYSTEM



1.3 Results and Discussion

The experimental results for the catalyst screening tests are shown in Table 3. All of the tests were conducted in the batch reactor system at identical operating conditions with the asphaltene-rich recycle liquid feed (NSRFC-A). Activity data are presented for pentane insolubles conversion (PIC), hydrogen content boost (HCB), hydrodenitrogenation (HDN) and hydrodesulphurization (HDS).

Pentane insolubles conversion ranged from 35.4% with Katalco 550S to 45.3% with Shell 317. This response variable represents the conversion of heavy coal liquids (asphaltenes and preasphaltenes) into oil. Four of the nine catalysts produced PI conversions in excess of 40%.

Hydrogen content boost ranged from 10.6% with Shell 324 to 14.6% with Shell 317. The measured levels of HCB and PIC for Kat-5000 were only marginally less than those for Shell 317. Both are nickel-molybdenum type catalysts. However, Shell 317 has a higher metals loading and a bimodal pore size distribution whereas Kat-5000 is a unimodal pore catalyst with a large surface area.

Denitrogenation ranged from 15.5% with Katalco 550S to 29.8% with Shell 317. Results for Shell 317 and Katalco 596 indicate that high nickel-molybdenum loading in combination with relatively large surface area promotes nitrogen removal.

Desulphurization ranged from 58.3% with Shell 324 to 71.7% with Shell 317. All of the catalysts exhibited relatively high initial activity for sulphur removal.

Shell 317 was found to be superior to the other catalysts in terms of overall performance. It registered the highest PIC, HCB, HDN and HDS activities. Additional experiments were carried out with Shell 317. The test results are presented in Table 4.

The effect of residence time on overall performance was investigated at 425°C and 20.68 MPa using the NSRFC-A feed. Increasing the residence time from 30 to 90 minutes affected significant gains in PIC, HCB, HDN and HDS as seen in Table 4 and Figure 3. Results were as follows:

- PIC increased from 38.9 to 51.0%
- HCB increased from 12.3 to 15.9%
- HDN increased from 19.1 to 33.3%
- HDS increased from 63.3 to 77.5%

Shell 317 was also examined at operating conditions similar to those employed in the second-stage catalytic reactor of the two-stage coal liquefaction bench unit. The reaction conditions were as follows: temperature 410°C; pressure 20.68 MPa; residence time 120 minutes. These conditions produced 53.5% PIC, 16.6% HCB, 35.7% HDN and 80.8% HDS as shown in Table 4.

Two catalytic hydroprocessing experiments were conducted with the asphaltene-lean recycle liquid (NSRFC-B). Amocat 1C and Shell 317 were used in these tests. The results presented in Table 4 confirm the superior performance of Shell 317. The levels of PIC, HCB, HDN and HDS determined with the NSRFC-B feed differ from those determined with the NSRFC-A feed. The deviations are most likely due to compositional differences between the feeds. In particular, to the nature and the quantities of the hydrocarbon types present and the structural environments in which the heteroatoms are bound.

TABLE 3

SUMMARY OF RESULTS FROM CATALYST SCREENING EXPERIMENTS

CATALYST	PRODUCT ANALYSES, WT. %				PIC	HCB	HDN	HDS
	PI	HYDROGEN	NITROGEN	SULPHUR	%	%	%	%
Amocat 1A	16.72	8.04	0.71	0.044	36.7	11.1	15.5	63.3
Amocat 1C	16.08	8.19	0.62	0.047	39.2	13.1	26.2	60.8
HPC 312	14.85	8.22	0.65	0.040	43.8	13.5	22.6	66.7
Katalco 550S	17.08	8.05	0.71	0.042	35.4	11.2	15.5	65.0
Katalco 596	15.91	8.16	0.61	0.048	39.8	12.7	27.4	60.0
Kat-5000	14.72	8.27	0.66	0.046	44.3	14.2	21.4	61.7
Shell 317	14.46	8.30	0.59	0.034	45.3	14.6	29.8	71.7
Shell 324	16.95	8.01	0.65	0.050	35.9	10.6	22.6	58.3
Cat-X	15.77	8.02	0.69	0.045	40.3	10.8	17.9	62.5

Reaction Conditions:

Temperature	425°C
Total Pressure	20.68 MPa
Time	60 Minutes

Feedstock Used: NSRFC-A Recycle Liquid

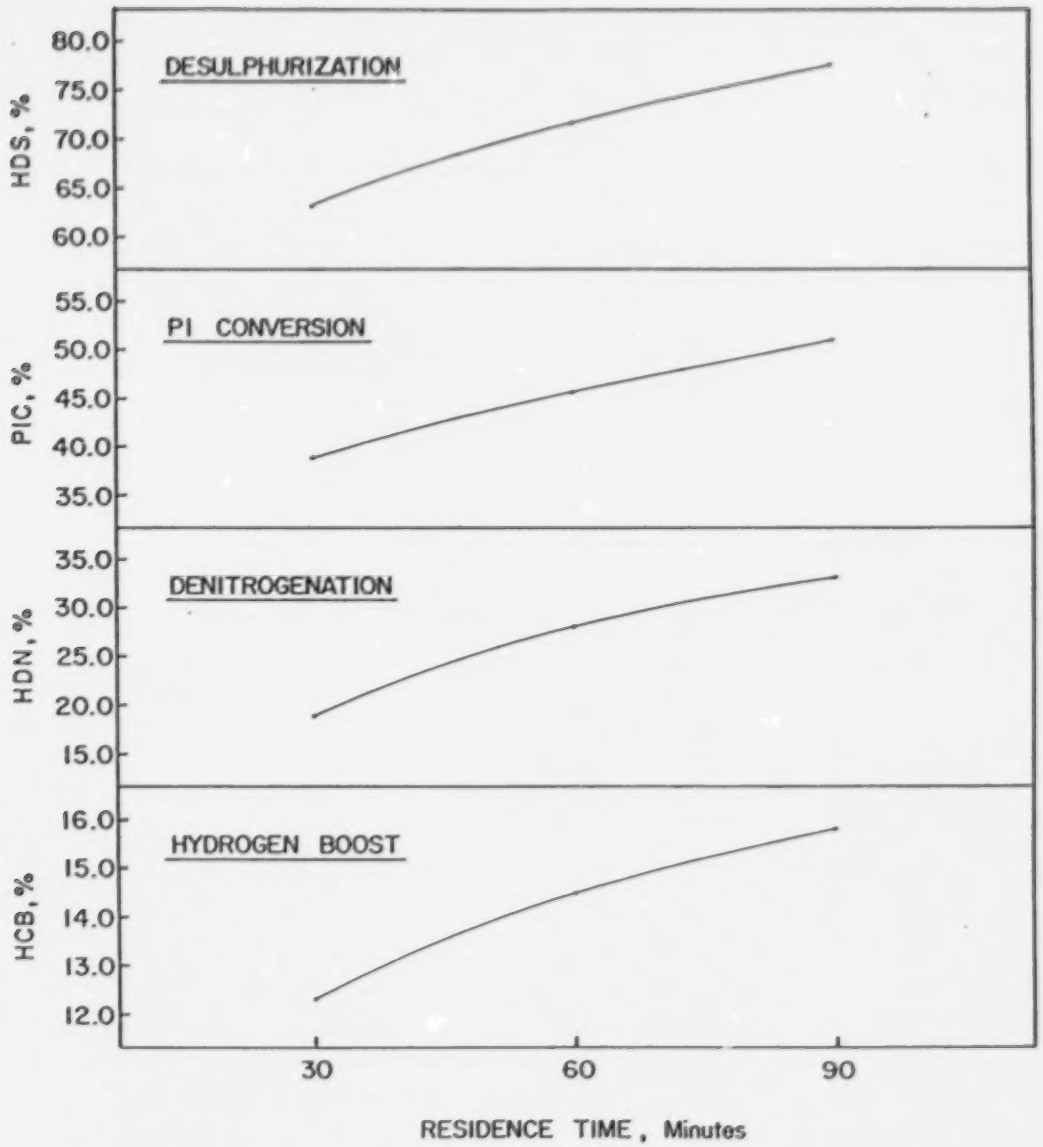
TABLE 4

RESULTS OF BATCH ACTIVITY TESTS WITH SHELL 317

CATALYST	REACTION TEMP, °C	RESIDENCE TIME, MINS.	PIC %	HCB %	HDN %	HDS %
Batch Tests with NSRFC-A Recycle Liquid						
Shell 317	425	30	38.9	12.3	19.1	63.3
Shell 317	425	60	45.3	14.6	29.8	71.7
Shell 317	425	90	51.0	15.9	33.3	77.5
Shell 317	410	120	53.5	16.6	35.7	80.8
Batch Tests with NSRFC-B Recycle Liquid						
Amocat 1C	425	60	56.0	3.0	17.9	40.0
Shell 317	425	60	69.3	6.6	30.4	47.5

Total Pressure: 20.68 MPa

Figure 3 - CATALYTIC ACTIVITIES OF SHELL 317 AS A FUNCTION OF RESIDENCE TIME



TASK 2 - CATALYST REGENERATION AND ACTIVITY TESTING

Catalytic upgrading of coal dissolution products is a vital part of two-stage liquefaction processing. The upgrading stage usually employs a sulphided nickel or cobalt-promoted molybdenum catalyst on an alumina support to increase the hydrogen to carbon ratio of the products and reduce their heteroatom content. In normal operations these catalysts experience a loss of activity with time.

The main causes of catalyst deactivation during coal liquefaction are the coverage of active sites by carbonaceous and metal deposits, pore-mouth blockage and changes in catalyst structure. It has been reported that carbonaceous material builds up very rapidly at the start of a coal liquefaction run with attendant catalyst deactivation. The contaminant metals accumulation occurs more slowly than the buildup of carbonaceous material and is responsible for a continued decline in activity after the carbon content has attained a relatively constant value. The most common contaminant metals are iron and titanium. Losses of active metal or promoter surface areas due to sintering are usually caused by prolonged exposure to high temperatures.

The objective of Task 2 was to establish the degree to which the activity of used coal liquefaction catalyst can be regenerated by controlled removal of carbonaceous deposits. The study involved extensive characterization of fresh, used and regenerated catalyst samples with regard to physical and chemical properties and batch activity testing to measure relative catalyst performance.

2.1 Used Catalysts Studied

Four aged Amocat 1C catalyst samples and one aged Katalco 550 sample were evaluated in this study. The samples were obtained from two-stage thermal/catalytic and catalytic/catalytic coal liquefaction bench unit operations at NSRFC. Used catalysts were removed from the system following a series of once-through experiments or after a long-term recycle liquefaction run. Catalyst was exposed to several coal feedstocks in the serial once-through experimental format whereas only one coal was processed in a typical recycle liquefaction test. Details pertaining to the operating history of the used samples are provided below.

Catalyst Identification	Catalyst Age[a]	Operating History
Amocat 1C	150	• Second-stage catalyst in catalytic/catalytic process configuration • Once-through operations with Lingan, Prince, Donkin and Illinois No. 6 coals (Run Nos. 8002-8016) • Operating temperature of catalyst, 425°C
Amocat 1C	518	• First-stage catalyst in catalytic/catalytic process configuration • Once-through operations with Lingan, Prince, Donkin and Illinois No. 6 coals (Run Nos. 8002-8016) • Operating temperature of catalyst ranged from 400 to 440°C
Katalco 550	145	• Second-stage catalyst in thermal/catalytic process configuration • Once-through operations with Lingan, Prince, Donkin and Illinois No. 6 coals (Run Nos. 6017-7006) • Operating temperature of catalyst ranged from 400 to 430°C
Amocat 1C	196	• Second-stage catalyst in thermal/catalytic process configuration • Recycle liquefaction run with Donkin coal (RCL-9100) • Operating temperature of catalyst ranged from 410 to 418°C
Amocat 1C	392	• Second-stage catalyst in thermal/catalytic process configuration • Recycle liquefaction run with Donkin coal (RCL-9200) • Operating temperature of catalyst, 410°C

[a] Catalyst age, kg coal/kg catalyst

2.2 Experimental Procedures

Before any used catalyst characterization, regeneration or activity testing began, a portion of each catalyst was extracted with organic solvent and then dried. Extractions were carried out in a Soxhlet extractor for 48 hours to remove adsorbed material and oil from the samples. All five used catalysts were extracted with tetrahydrofuran (THF). Four of the five samples were also extracted with toluene to determine if the choice of solvent affects subsequent analyses. Amocat 1C used in the first-stage reactor in Run Nos. 8002-8016 was not extracted with toluene because it had been washed earlier with THF.

Following extraction, selected used catalysts were regenerated by controlled oxidation to remove carbonaceous deposits. The "carbon burnoff" regeneration experiments were carried out in the downflow tubular reactor system shown in Figure 1. The selected samples were regenerated by heating approximately 30 g at 454°C in a flowing oxygen/nitrogen mixture. The reactor temperature was increased slowly such that the bulk temperature of the extrudates did not exceed 454°C. The heat-up time was typically about 12 hours. Samples were held at temperature for periods of 24 or 48 hours. The flowrate of the 10 mol % oxygen in nitrogen mixture was maintained at 2.2 L/min in carbon burnoff operations.

After carbon burnoff, each sample was sulphided and then subjected to batch activity testing in accordance with the procedures described in Section 1.2. In addition, the activities of fresh sulphided and aged catalyst samples were also evaluated. The reaction conditions used for activity testing were the same as those used in the catalyst screening experiments.

The fresh, used (after extraction) and regenerated (after carbon burnoff) catalyst samples were analyzed for active metals by using atomic absorption spectroscopy and for carbon, hydrogen, nitrogen and sulphur by using established procedures. Iron, titanium and calcium quantitative analyses were carried out by using atomic absorption spectroscopy. Surface areas were measured by the BET adsorption method with nitrogen. Pore volumes and pore volume distribution were determined by mercury porosimetry.

In order to simplify the presentation of data; the fresh, used and regenerated catalyst samples were coded using a letter-number system. Descriptions of the coded samples are presented in Table 5.

TABLE 5

REFERENCE CODE USED FOR FRESH, AGED AND REGENERATED CATALYST SAMPLES TESTED

CATALYST SAMPLE	DESCRIPTION
A-1	Fresh Amocat 1C
A-2	Aged Amocat 1C from 2nd stage reactor after Runs 8002-8016, toluene extracted
A-3	Aged Amocat 1C from 2nd stage reactor after Runs 8002-8016, THF extracted
A-4	Regenerated Amocat 1C, catalyst A-2 after carbon burnoff (24 hrs)
B-3	Aged Amocat 1C from 1st stage reactor after Runs 8002-8016, THF extracted
B-4	Regenerated Amocat 1C, catalyst B-3 after carbon burnoff (24 hrs)
C-1	Fresh Katalco 550
C-2	Aged Katalco 550 from 2nd stage reactor after Runs 6017-7006, toluene extracted
C-3	Aged Katalco 550 from 2nd stage reactor after Runs 6017-7006, THF extracted
C-4	Regenerated Katalco 550, catalyst C-2 after carbon burnoff (24 hrs)
D-2	Aged Amocat 1C from 2nd stage reactor after RCL-9100, toluene extracted
D-3	Aged Amocat 1C from 2nd stage reactor after RCL-9100, THF extracted
D-4	Regenerated Amocat 1C, catalyst D-2 after carbon burnoff (24 hrs)
D-5	Regenerated Amocat 1C, catalyst D-3 after carbon burnoff (24 hrs)
D-6	Regenerated Amocat 1C, catalyst D-2 after carbon burnoff (48 hrs)
E-2	Aged Amocat 1C from 2nd stage reactor after RCL-9200, toluene extracted
E-3	Aged Amocat 1C from 2nd stage reactor after RCL-9200, THF extracted
E-6	Regenerated Amocat 1C, catalyst E-2 after carbon burnoff (48 hrs)
E-7	Regenerated Amocat 1C, catalyst E-3 after carbon burnoff (48 hrs)

Catalyst Age, kg coal/kg catalyst:

A-2 & A-3	=	150
B-3	=	518
C-2 & C-3	=	145
D-2 & D-3	=	196
E-2 & E-3	=	392

2.3 Results and Discussion

The results of the chemical analyses performed on fresh, used and regenerated catalyst samples are summarized in Table 6. The samples were coded using a letter-number system. Descriptions of the coded samples are provided in the previous section. Elemental analyses included; carbon, hydrogen, nitrogen, sulphur, active metals (nickel, molybdenum, tungsten) and contaminant metals (iron, calcium, titanium).

Carbon results show that all five used catalysts have substantial carbonaceous deposits. Sample D-2 (Amocat 1C from RCL-9100) had the highest carbon content, 20.3%. Whereas, the carbon content of sample E-2 (Amocat 1C from RCL-9200) was a much lower 12.4%, in spite of higher coal throughput per unit weight of catalyst. Two process features are believed to have influenced the lower degree of carbon deposition in RCL-9200. Firstly, solvent deasphalting was applied to the recycle liquid to prevent the buildup of heavy asphaltenic components in this stream. Secondly, the catalytic reactor was operated at a relatively low temperature, 410°C, throughout the run.

In the carbon burnoff experiments with used Amocat 1C from RCL-9100, sample D-6 had a lower carbon content than sample D-4. Used catalyst, after extraction with toluene, was held at the maximum carbon burnoff temperature (454°C) for 48 hours in the former case compared with 24 hours in the latter. By extending the final burnoff time from 24 to 48 hours, the carbon content of the used catalyst was reduced from 0.54% to 0.07%.

Iron, titanium and calcium results indicate that the total accumulation of contaminant metals was rather low in all cases. It is interesting to note that iron accumulated to a greater extent than the other contaminant metals. The highest iron concentration, 1.07%, was measured on sample B-4, Amocat 1C at an age of 518 kg coal/kg catalyst after regeneration. This sample also contained the highest level of titanium, 0.25%. Low levels of calcium were detected in the aged catalysts, typically in the 20 - 50 ppm range.

Table 7 presents the results of the physical characterization work performed on fresh, used and regenerated catalyst samples. Bulk density, pore volume, surface area and modal pore size distribution data are presented. The used catalysts had lower pore volumes and surface areas than fresh catalyst. However, these features were restored to a significant degree in the regenerated samples.

The porosity and surface area changes in each group are consistent with expectations. For example, in Group A the effect of surface coke deposits can be observed by comparing A-1 with A-2 and A-3. Total pore volume was reduced by about 40% and the BET surface area by about 25%. The average diameter of the small mesopore mode also decreased. Upon regeneration, A-4 shows restoration of most of the original porosity features. Compared with A-1, the total pore volume is 105% whereas the surface area is 94% of the original. Both coincide with the growth of the median pore diameter in the small mesopore range, which can be caused by slight sintering.

A relatively large loss of porosity is apparent when comparing samples C-1 and C-2. Total pore volume and surface area were reduced by 48% and 34% respectively. About 96% of the pore volume but only 76% of the surface area was restored in the regenerated sample C-4. It is important to note, however, that the carbon burnoff period for C-4 was only 24 hours. A longer burnoff period is expected to restore more of the surface area as evidenced by comparing samples D-4 and D-6.

Surface characterization of sample E-2 revealed that Amocat 1C experienced pore volume and surface area losses of 34% and 35% respectively in RCL-9200. After carbon burnoff for 48 hours, the pore volume of the regenerated sample E-6 was 107% of the original whereas the surface area was 86%. Samples E-2 and E-6 had a larger mean diameter in the macropore mode than the fresh catalyst, A-1. The increase in the mean diameter of the macropore mode is possibly due to prolonged exposure of the catalyst to high temperature in the presence of water during coal liquefaction operations.

Results of the batch activity tests on fresh, used and regenerated catalyst samples are given in Table 8. Feed and product liquids were analyzed to determine relative catalytic activity for PIC, HCB, HDN and HDS. The used catalysts showed activity losses for all functionalities. Regenerating the used catalysts yielded significant improvements in all four activities.

It is apparent from the data presented in Table 8 that the five used catalysts experienced severe deactivation. Sample C-3, used Katalco 550 extracted with THF, showed

the greatest activity losses for all functionalities. Compared with C-1, decreases in PIC, HCB, HDN and HDS ranged from 31% to 100% as seen in Table 9. Regeneration of the used catalyst resulted in significant recoveries of all four activities as illustrated in Figure 4. Actual recoveries in sample C-4 ranged from 84% to 100% of the original activities.

Similar trends in activity losses and recoveries were measured for used Amocat 1C in groups A, B, D and E (see Table 9). It is interesting to note that in the 20-day recycle coal liquefaction run catalytic activity losses for PIC, HCB, HDN and HDS ranged from 29% to 68%. Upon regeneration, E-6 showed recoveries ranging from 73% to 98% of the original activities with PIC, HCB and HDS all exceeding 80% as shown in Figure 5.

The results of this study indicate that catalyst deactivation is primarily due to the buildup of carbonaceous deposits. Carbonaceous deposits cause deactivation presumably due to active-site coverage and yield a decrease in catalyst average pore size due to the filling of larger pores. The physical properties (i.e.; total pore volume, BET surface area, average pore diameter and density) of the used catalysts were restored to a large degree via controlled carbon burnoff. Although this procedure did not restore catalyst to its original state, the degree of restoration is high enough to warrant further evaluation of the concept in larger scale operations.

TABLE 6

CHEMICAL ANALYSES OF FRESH, USED AND REGENERATED CATALYSTS

CATALYST SAMPLE	NiO Wt. %	MoO_3 Wt. %	WO_3 Wt. %	Fe Wt. %	Ti Wt. %	Ca ppm	CARBON Wt. %	HYDROGEN Wt. %	NITROGEN Wt. %	SULPHUR Wt. %
A-1	2.89	16.09	-	0.08	0.02	12	0.14	0.12	0.01	0.14
A-2	2.22	13.83	-	0.57	0.14	21	14.51	1.23	0.40	5.36
A-3	2.18	13.40	-	0.53	0.14	24	13.23	1.14	0.39	5.44
A-4	2.67	16.01	-	0.70	0.19	28	0.46	0.32	0.02	0.49
B-3	2.12	12.99	-	0.88	0.20	34	13.17	1.33	0.37	5.52
B-4	2.27	15.53	-	1.07	0.25	44	0.59	0.31	ND	0.56
C-1	3.58	-	17.5	0.05	0.05	40	0.20	0.20	0.02	0.16
C-2	2.95	-	13.9	0.93	0.10	53	14.12	1.14	0.40	5.92
C-3	3.13	-	15.0	0.93	0.10	52	12.48	1.12	0.35	5.91
C-4	3.46	-	17.0	1.02	0.10	74	0.48	0.33	0.03	0.88
D-2	1.71	13.34	-	0.20	0.03	18	20.33	1.23	0.41	5.38
D-3	1.85	13.53	-	0.18	0.02	16	19.64	1.20	0.40	5.07
D-4	2.58	15.88	-	0.25	0.03	18	0.54	0.29	0.03	0.52
D-5	2.62	15.92	-	0.25	0.03	17	0.20	0.18	0.03	0.60
D-6	2.53	16.00	-	0.30	0.03	23	0.07	0.29	ND	0.54
E-2	1.84	13.17	-	0.18	0.02	20	12.43	1.21	0.26	6.00
E-3	1.91	12.98	-	0.20	0.03	19	12.15	1.18	0.26	6.13
E-6	2.47	15.98	-	0.21	0.05	31	0.13	0.13	0.03	0.69
E-7	2.48	15.90	-	0.20	0.04	34	0.14	0.35	0.02	0.66

TABLE 7

PHYSICAL CHARACTERISTICS OF FRESH, USED AND REGENERATED CATALYSTS

CATALYST SAMPLE	BULK DENSITY, g/ml	PORE VOLUME, ml/g	SURFACE AREA, m^2/g	V_L %	V_M %	MODES A°
A-1	0.64	0.61	185	15	85	100,700
A-2	0.83	0.35	140	20	80	80,700
A-3	0.83	0.37	140	19	81	90,700
A-4	0.65	0.64	173	15	85	120,700
B-3	0.84	0.35	144	19	81	70,600
B-4	0.65	0.59	159	15	85	100,800
C-1	0.77	0.48	192	6	94	80, -
C-2	0.97	0.25	126	11	89	50, -
C-3	0.98	0.28	132	8	92	60, -
C-4	0.83	0.46	146	8	92	100, -
D-2	0.89	0.29	112	21	79	80,500
D-3	0.89	0.31	132	24	76	80,500
D-4	0.64	0.64	145	17	83	110,700
D-5	0.66	0.64	135	17	83	120,600
D-6	0.65	0.62	159	16	84	110,700
E-2	0.81	0.40	120	22	78	100,1000
E-6	0.63	0.65	160	15	85	100,1000

SURFACE AREA - BET specific surface area by nitrogen adsorption
V_L - percentage of macropore volume
V_M - percentage of mesopore volume
MODES - modal distribution within mespores and macropores, mean diameter

TABLE 8

RESULTS OF ACTIVITY TESTS ON FRESH, USED AND REGENERATED CATALYSTS

CATALYST SAMPLE	PRODUCT ANALYSES, WT. %				PIC %	HCB %	HDN %	HDS %
	PI	HYDROGEN	NITROGEN	SULPHUR				
A-1	16.08	8.19	0.62	0.047	39.2	13.1	26.2	60.8
A-2	20.13	7.77	0.80	0.059	23.8	7.3	4.8	50.8
A-3	20.73	7.69	0.82	0.061	21.6	6.2	2.4	49.2
A-4	17.29	8.09	0.68	0.052	34.6	11.7	19.0	56.7
B-3	20.09	7.76	0.82	0.057	24.0	7.2	2.4	52.5
B-4	17.12	8.10	0.69	0.052	35.2	11.9	17.9	56.7
C-1	15.97	8.17	0.71	0.046	39.6	12.8	15.5	61.7
C-3	22.22	7.52	0.84	0.069	15.9	3.9	0.0	42.5
C-4	16.72	8.02	0.71	0.046	36.7	10.8	15.5	61.7
D-3	20.36	7.71	0.82	0.064	23.0	6.5	2.4	46.7
D-4	15.70	8.16	0.68	0.047	40.6	12.7	19.0	60.8
D-5	16.40	8.20	0.68	0.046	37.9	13.3	19.0	61.7
D-6	15.62	8.14	0.68	0.048	40.9	12.4	19.0	60.0
E-2	20.30	7.87	0.77	0.068	23.2	8.7	8.3	43.3
E-6	16.26	8.06	0.68	0.060	38.5	11.3	19.0	50.0

TABLE 9

SUMMARY OF CATALYTIC ACTIVITY LOSS AND RECOVERY DATA

USED CATALYST	ACTIVITY LOSS, %			
	PIC	HCB	HDN	HDS
A-2	39.3	44.3	81.7	16.4
B-3	38.8	45.0	90.8	13.7
C-3	59.8	69.5	100.0	31.1
D-3	41.3	50.4	90.8	23.2
E-2	40.8	33.6	68.3	28.8

REGENERATED CATALYST	% OF INITIAL ACTIVITY			
	PIC	HCB	HDN	HDS
A-4	88.3	89.3	72.5	93.3
B-4	89.8	90.8	68.3	93.3
C-4	92.7	84.4	100.0	100.0
D-6	104.3	94.7	72.5	98.7
E-6	98.2	86.3	72.5	82.2

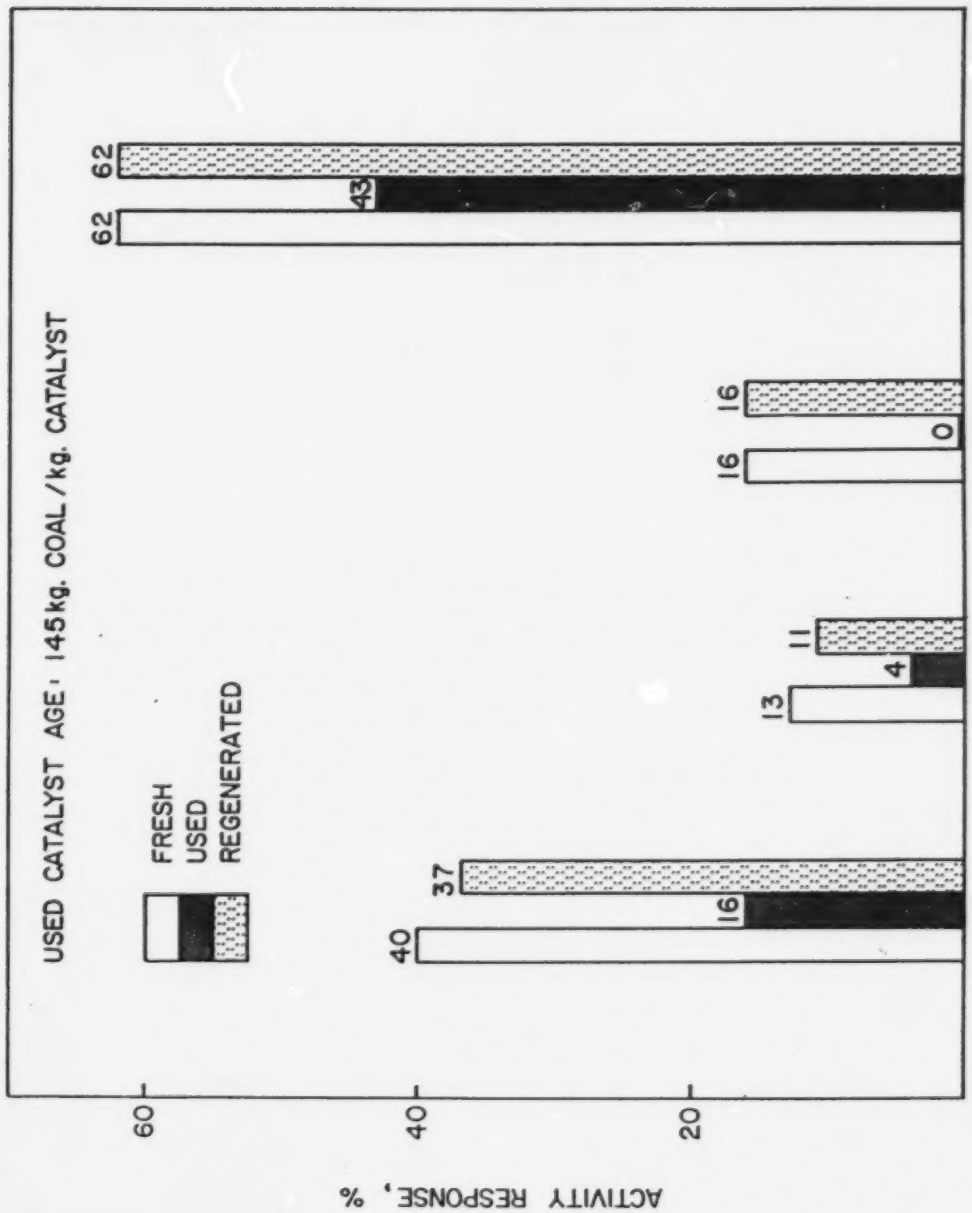


Figure 4 - ACTIVITY COMPARISONS OF FRESH, USED AND REGENERATED KATALCO 550 CATALYST

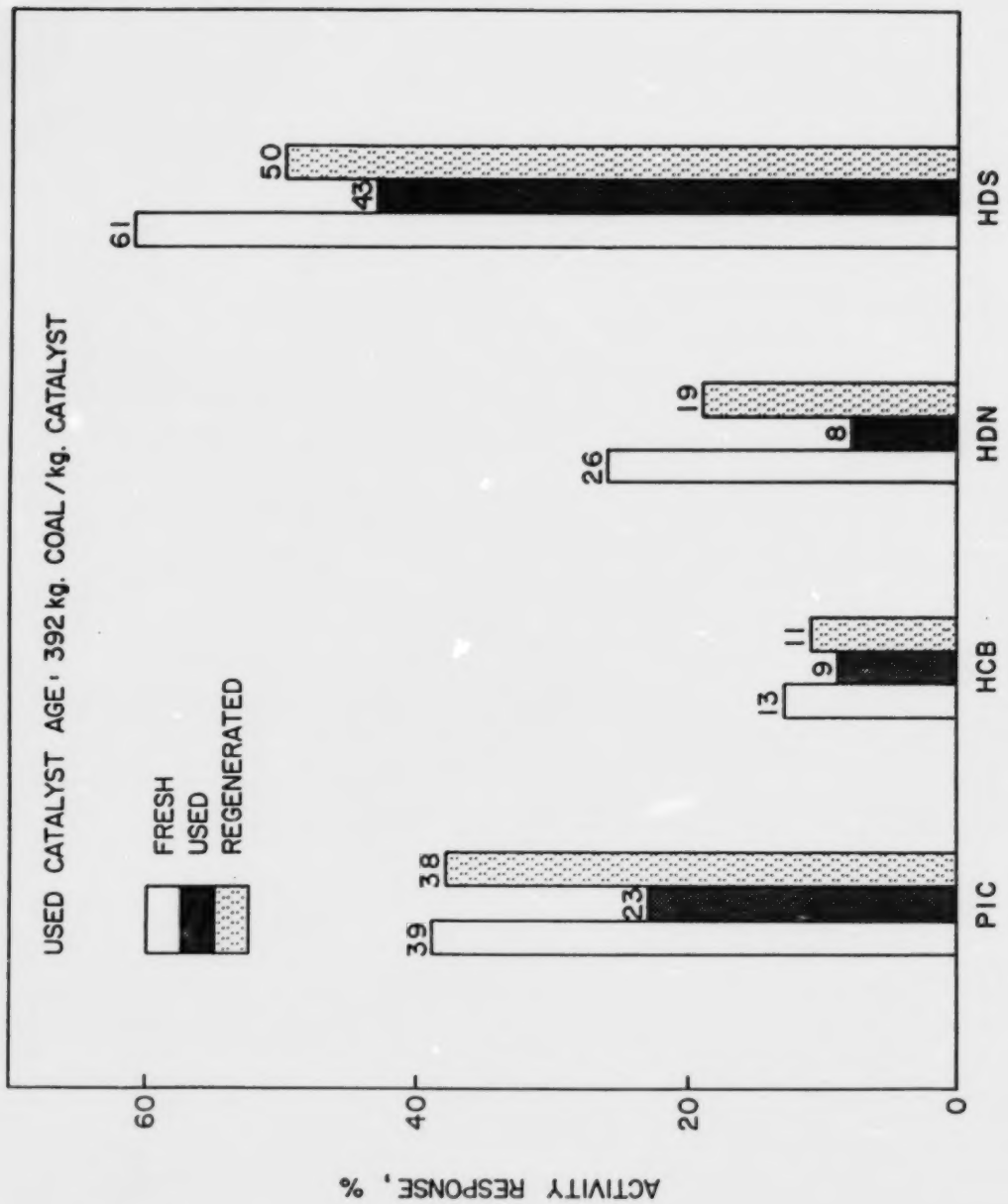


Figure 5 - ACTIVITY COMPARISONS OF FRESH, USED AND REGENERATED AMOCAT IC CATALYST

TASK 3 - PROCUREMENT OF NEW EQUIPMENT

The purpose of this task was to procure and install new equipment for use in the asphaltene conversion and catalyst regeneration studies. Two major purchases were made, a bench-top stirred autoclave and a laboratory tube furnace. Details pertaining to the new equipment are given below.

The first item, a 300 cc Robinson-Mahoney style reactor complete with furnace and temperature controller was purchased from AE Autoclave of Canada Limited. The reactor internals include a static catalyst basket and an axial impeller system. The reactor was used for catalyst activity testing in Tasks 1 and 2.

The laboratory tube furnace, Lindberg Model 54352 was purchased with a programmable temperature controller. The furnace is suitable for reaction tubes up to 6.35 cm in diameter. The temperature controller has a maximum of 8 ramp and soak cycles. This equipment was procured for catalyst sulphiding operations and carbon burnoff experiments.

TASK 4 - PREPARATION OF COAL FEEDSTOCKS

Four coal feedstocks were used in the two-stage liquefaction experiments presented in Task 6. Bench-scale testing was concentrated on three Nova Scotia high volatile bituminous coals; Donkin Harbour, Lingan Harbour and Prince Hub. Limited test work was conducted on a high volatile American coal, Illinois No. 6. The Sydney area coals were provided courtesy of the Cape Breton Development Corporation. Illinois No. 6 coal from the Burning Star Mine was procured through Cepheus Industries Incorporated, Marion, Illinois. Preparation of the coals involved riffling, grinding and screening. After screening, the individual coals were thoroughly mixed and stored in plastic-lined drums with a nitrogen blanket.

Proximate and ultimate analyses of the coals are given in Table 10. Proximate analysis, free-swelling index and forms of sulphur were determined according to standard methods. Total sulphur was measured using a Leco sulphur analyzer. Carbon, hydrogen and nitrogen were determined using a Leco elemental analyzer.

Petrographic analyses of the four coals is given in Table 11. These analyses were carried out courtesy of the Atlantic Geoscience Center, G.S.C., Dartmouth, Nova Scotia.

TABLE 10

ANALYSES OF COALS TESTED

COAL DESCRIPTION:	LINGAN HR-9	DONKIN HR-10	PRINCE HB-9	ILLINOIS NO. 6
Moisture, Wt. %	0.95	2.14	2.91	3.23
PROXIMATE (Dry Basis) Wt. %				
Ash	4.18	6.01	7.20	9.75
Volatile Matter	35.23	35.95	37.36	40.97
ULTIMATE (Dry Basis) Wt. %				
Carbon	80.13	78.80	73.88	69.64
Hydrogen	5.45	5.01	4.95	4.94
Nitrogen	1.27	1.36	1.31	1.46
Sulphur	2.00	2.55	3.46	2.89
Ash	4.18	6.01	7.20	9.75
Oxygen (by difference)	6.97	6.27	9.20	11.32
SULPHUR FORMS (Dry Basis) Wt. %				
Sulphate	0.04	0.12	0.14	0.04
Pyritic	1.49	1.27	2.38	1.17
Organic (by difference)	0.47	1.16	0.94	1.68
Total	2.00	2.55	3.46	2.89
FREE SWELLING INDEX	7½	7½	6½	2½
HEATING VALUE (kj/kg)	34,162	32,260	30,393	28,652

TABLE 11

PETROGRAPHIC CHARACTERISTICS OF COALS TESTED

COAL DESCRIPTION:	LINGAN HR-9	DONKIN HR-10	PRINCE HB-9	ILLINOIS NO. 6
MACERAL COMPOSITION (% by volume)				
Vitrinite	73.2	80.0	78.4	75.6
Exinite	4.2	5.4	4.6	4.4
Inertinite	19.6	12.0	11.8	12.4
Macrinite	(2.8)	(2.0)	(1.4)	(1.2)
Micrinite	(4.2)	(2.8)	(1.6)	(2.2)
Semifusinite	(5.2)	(3.8)	(5.0)	(3.4)
Fusinite	(7.4)	(3.4)	(3.8)	(5.6)
Mineral Matter	3.0	2.6	5.2	7.6
Pyrite	(0.4)	(2.2)	(2.6)	(1.8)
Quartz	(0.2)	(0.2)	(0.2)	(1.4)
Shale	(2.4)	(0.2)	(2.4)	(4.4)
% R_o Max.	0.98	0.94	0.74	0.60
V-Type Distribution, %				
V5	-	-	-	44
V6	-	-	22	56
V7	-	-	62	-
V8	10	18	16	-
V9	46	74	-	-
V10	42	8	-	-
V11	2	-	-	-

TASK 5 - EQUIPMENT MAINTENANCE

Actual work associated with Task 5 included inspection and general maintenance of the hydrogen compression facility, the fixed-bed catalytic hydrotreater and the two-stage coal liquefaction unit. These activities are essential to ensure safe working conditions and reliable operating systems.

In the hydrogen compression and storage area scheduled maintenance was carried out on the single-stage diaphragm compressor. The design capacity of this 7.5 horsepower unit is 114 L/min from 3.5 MPa to 34.5 MPa. Routine maintenance involved cleaning filters, replacing the hydraulic fluid and checking the tension on drive belts. The triple diaphragm assembly and o-ring seals were also replaced during the maintenance period.

The fixed-bed hydrotreater used to produce reaction solvent for coal liquefaction experiments has been described in an earlier report (3). On turnaround, the high pressure liquid metering pump and the vacuum pump used regularly with this system were given a general overhaul. Liquid transfer lines between the feed vessel and the reactor inlet were removed and cleaned. Used catalyst in the tubular reactor was replaced with fresh material. Following this, new heating tapes and insulation were installed on all of the heat traced lines. In addition, high pressure block valves on both feed and product vessels were replaced due to wear associated with normal usage.

A brief description of the two-stage coal liquefaction unit is presented in Appendix A. Most of the work associated with Task 5 was related to mechanical maintenance of this unit. Worn internal components of the second-stage catalytic reactor, in particular the lower drive shaft and the bearing in the base weldment, were replaced at NSRFC's machine shop. Several other parts on the rig were also replaced including: all rupture discs, worn high pressure block valves and frayed high temperature insulation. Product let-down valves were inspected and worn parts were replaced. Wet test meters were thoroughly cleaned and then performance tested.

TASK 6 - INTEGRATED TWO-STAGE LIQUEFACTION

The objective of Task 6 was to evaluate the performance of Shell 317 in two-stage liquefaction operations with Nova Scotia coals. A series of integrated thermal/catalytic experiments was carried out with this nickel-molybdenum bimodal catalyst. The tests were conducted in a once-through processing mode using hydrogenated anthracene oil as reaction solvent. Details of the experimental work are presented in the following sections.

6.1 Preparation of Reaction Solvent

Reaction solvent for the coal liquefaction test work was prepared from raw anthracene oil. The raw oil is a coal-tar distillate which contains ca. 5.3 wt. % hydrogen. It was supplied by Domtar Chemicals Limited (Hamilton, Ontario).

Characteristics of the raw oil are given in Table 12. Carbon and hydrogen were determined using a Leco elemental analyzer. A standard kjeldahl method was used for the determination of nitrogen. Total sulphur content was measured using x-ray fluorescence.

In this study, the hydrogen aromatic/aliphatic distribution was established by proton nuclear magnetic resonance (H-NMR). A Varian EM360L continuous wave spectrometer operating in the Fourier transform mode at 60 MHZ was used to obtain H-NMR spectra. Proton assignments were as follows: aromatic hydrogens (H_{ar}) were found in the region of 9 - 6 ppm. Benzylic hydrogens including methyls, occur at 3.5 to 2 ppm (H_{α}). Hydrogen,

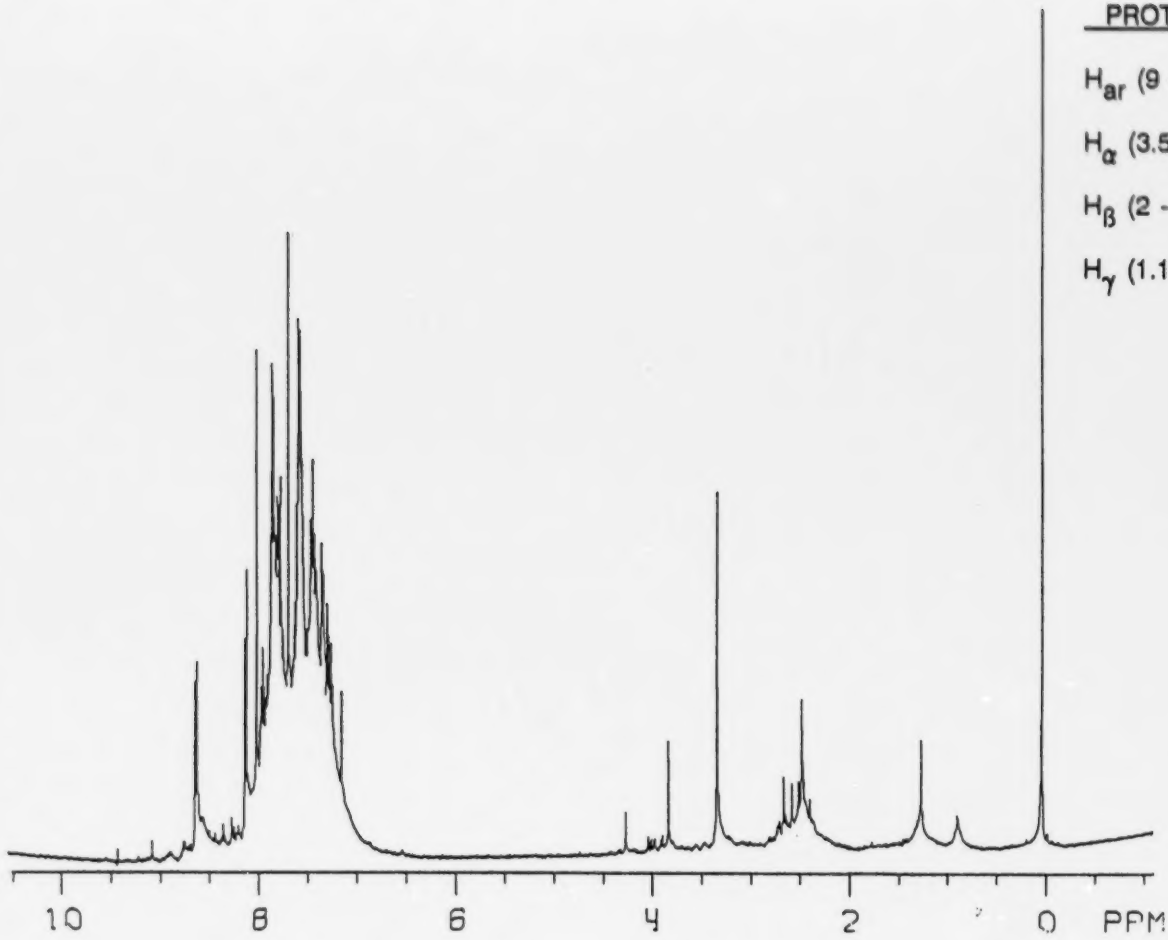
except methyls, on carbons one or more positions removed from the aromatic rings occur at 2 - 1.1 ppm (H_β). Aliphatic methyls are found at 1.1 - 0.4 ppm (H_γ). As almost no long aliphatic side chains are believed to be present, the H_β protons are predominantly in rings. These assignments are consistent with similar analyses reported in the literature (13, 14). Figure 6 is a typical H-NMR spectrum of raw anthracene oil.

TABLE 12

ANALYSIS OF RAW ANTHRACENE OIL

SAMPLE DESCRIPTION:	BATCH NO. 8-21
Specific Gravity, 60/60°F	1.1601
Carbon, Wt. %	91.52
Hydrogen, Wt. %	5.33
Nitrogen, Wt. %	1.04
Sulphur, Wt. %	0.55
Proton Distribution, %	
H_{ar} (9 - 6 ppm)	87.61
H_{α} (3.5 - 2 ppm)	8.06
H_{β} (2 - 1.1 ppm)	2.99
H_{γ} (1.1 - 0.4 ppm)	1.34
Distillation Data, °C (ASTM D-1160)	
IBP	218
10%	314
20%	329
30%	343
40%	353
50%	361
60%	373
70%	387
80%	410
90%	441
95%	466
EP	506

Figure 6 - H-NMR SPECTRA OF RAW ANTHRACENE OIL WITH 5.33 WT. % HYDROGEN



PROTON DISTRIBUTION, %	
H_{ar} (9 - 6 ppm)	87.61
H_{α} (3.5 - 2 ppm)	8.06
H_{β} (2 - 1.1 ppm)	2.99
H_{γ} (1.1 - 0.4 ppm)	1.34

NSRFC's fixed-bed catalytic hydrotreater was employed to prepare reaction solvent from the raw oil. A commercial cobalt-molybdenum hydrotreating catalyst, Nalcomo 479, was used to produce solvent containing 9% hydrogen. The operating conditions for raw oil hydrogenation are summarized in Table 13. The characteristics of a 9% H oil blend are shown in Table 14. An H-NMR spectrum of 9% H solvent is presented in Figure 7.

Approximately 100 liters of 9% H reaction solvent was produced to meet the requirements of the coal liquefaction test program. The solvent was produced at the rate of 1.8 liters per 7-hour shift. Daily production was collected to obtain 20-liter batches. Analyses of the individual batches are presented in Table 15. These batches were blended with about 25 liters of 9% H solvent on hand from previous hydrotreating operations. The analysis given in Table 14 is representative of the blend.

TABLE 13

REACTION CONDITIONS FOR ANTHRACENE OIL HYDROGENATION

Reactor Temperature, °C	366 - 373
Reactor Pressure, MPa	15.51
LHSV, hr^{-1}	0.20
Hydrogen Vented, L/hr	18 - 30
Product Hydrogen Content, Wt. %	9.0

Catalyst Used: Nalcomo 479

TABLE 14

CHARACTERISTICS OF REACTION SOLVENT

SAMPLE DESCRIPTION:	HAO - 101
Specific Gravity, 60/60°F	1.0351
Carbon, Wt. %	90.67
Hydrogen, Wt. %	8.96
Nitrogen, Wt. %	0.20
Sulphur, Wt. %	0.120
Proton Distribution, %	
H_{ar} (9 - 6 ppm)	23.66
H_{α} (3.5 - 2 ppm)	25.24
H_{β} (2 - 1.1 ppm)	37.84
H_{γ} (1.1 - 0.4 ppm)	13.26
Distillation Data, °C (ASTM D-1160)	
IBP	197
10%	253
20%	273
30%	285
40%	300
50%	308
60%	318
70%	331
80%	350
90%	373
95%	387
EP	457

Figure 7 - H-NMR SPECTRA OF HYDROGENATED ANTHRACENE OIL WITH 8.96 WT. % HYDROGEN

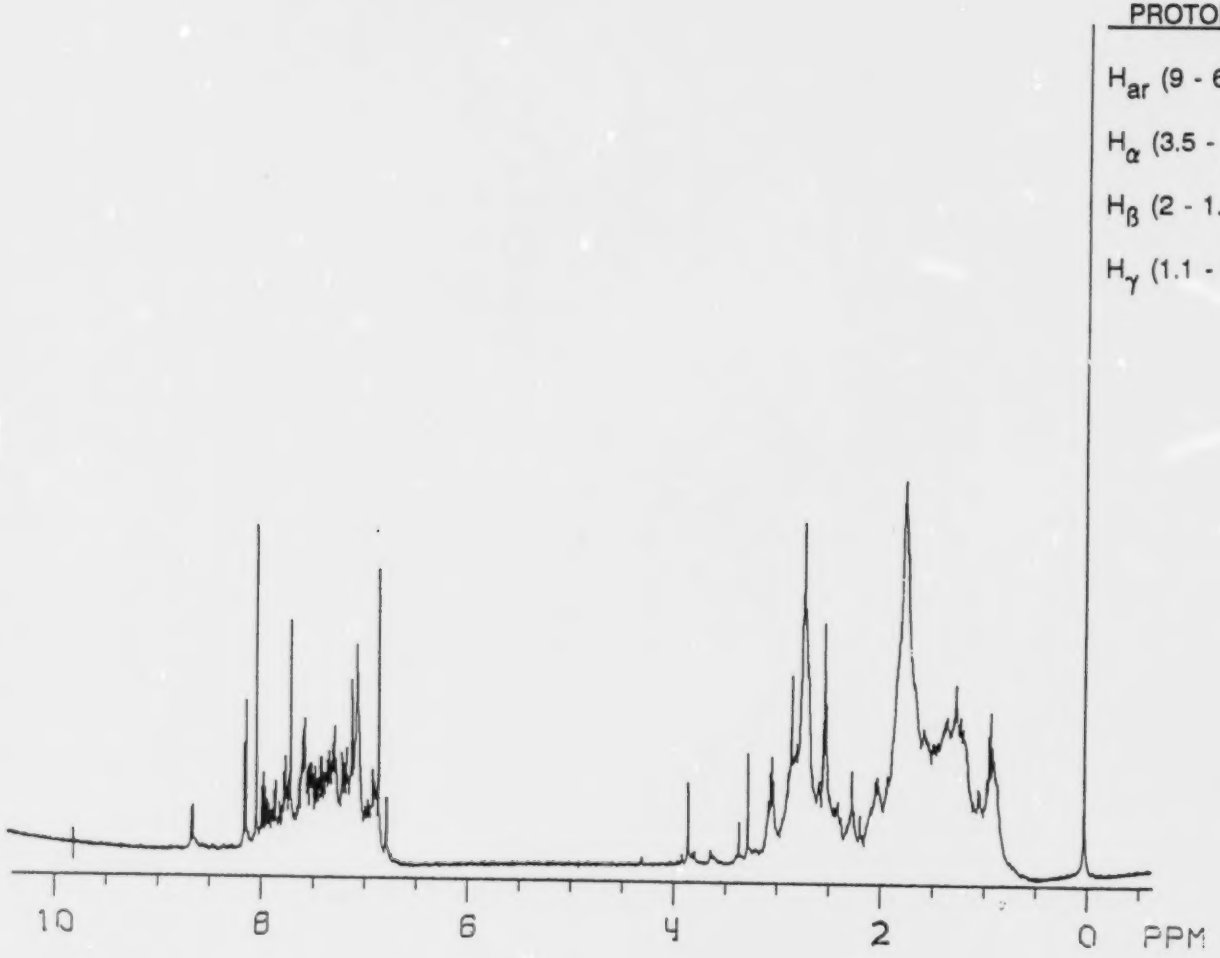


TABLE 15

ANALYSES OF 20-LITER BATCHES OF 9% H SOLVENT

BATCH NO.	1	2	3	4	5
Specific Gravity, 60/60°F	1.0321	1.0345	1.0352	1.0371	1.0381
Carbon, Wt. %	90.73	90.63	90.62	90.67	90.76
Hydrogen, Wt. %	8.97	8.99	8.93	8.97	8.91
Nitrogen, Wt. %	0.14	0.17	0.18	0.18	0.21
Sulphur, Wt. %	0.010	0.010	0.010	0.010	0.010
Proton Distribution, %					
H_{ar} (9 - 6 ppm)	23.32	22.68	22.71	23.55	24.06
H_{α} (3.5 - 2 ppm)	24.09	24.13	24.42	23.67	23.74
H_{β} (2 - 1.1 ppm)	40.70	39.99	39.88	38.98	38.94
H_{γ} (1.1 - 0.4 ppm)	11.89	13.21	12.99	13.81	13.20
Distillation Data, °C (ASTM D-86)					
IBP	163	181	187	180	180
5%	252	260	260	260	260
10%	269	277	275	277	276
20%	292	296	296	297	298
30%	306	310	310	310	309
40%	315	318	318	320	318
50%	326	328	327	330	329
60%	337	340	339	340	340
70%	349	352	352	353	353
80%	366	370	370	370	370
90%	390	394	397	396	394
95%	410	415	420	418	419
EP	489	508	503	505	484

6.2 Two-Stage Thermal/Catalytic Liquefaction with Shell 317

Two-stage bench unit operations with Shell 317 nickel-molybdenum bimodal catalyst began in July, 1989. The experimental work was undertaken because Shell 317 exhibited superior performance relative to the other catalysts evaluated in Task 1.

A schematic diagram of the two-stage bench unit used is shown in Appendix A. On completion of the planned maintenance, the system was reassembled with 0.33 kg of Shell 317 in the second-stage reactor. The rig was then pressure tested at 17.24 MPa at room temperature. Following this a trial run was made with oil alone to verify the operational status of mechanical and electrical systems.

Prior to initiating coal liquefaction experiments, a 30-hour run was carried out to sulphide the fresh catalyst using hydrogenated anthracene oil, 7.5% H, spiked with dimethyl disulphide. The sulphiding procedure was conducted at 17.24 MPa and a start-of-run temperature of 175°C. Temperature was increased gradually over a 24-hour period to a maximum of 370°C.

A total of ten two-stage thermal/catalytic liquefaction experiments were completed under Task 6.2. Test work was concentrated on Harbour and Hub seam coals from the Sydney coalfield. One run was carried out with Illinois No. 6 coal for comparative purposes. The experiments were conducted in a once-through processing mode using hydrogenated anthracene oil containing 9% H as reaction solvent. In most of the experiments,

coal concentration in the feed slurry was fixed at 28 wt. %. Hydrogen treatrate was ca. 20 wt. % based on dry coal.

A typical coal liquefaction run was of 10 hours duration. However, an additional 12 hours was required for preliminary and post run operations. In the majority of runs the controlled variables lined-out about 4 - 5 hours after start-up. During the steady state operating period, vent gas streams were sampled and other product streams were collected for analytical and material balance purposes.

In the experiments described hereafter, the following definitions for the product fractions isolated by solvent extraction were used:

oil - pentane solubles

asphaltenes - toluene solubles, pentane insolubles

preasphaltenes - THF solubles, toluene insolubles

A direct extraction technique was used to determine these fractions. Individual samples of the product were separately extracted with pentane, toluene and tetrahydrofuran (THF). Conversions were calculated on the basis of maf coal fed to the reaction zone during the steady state sampling period and unconverted coal in the dry insoluble residues. Conversion calculations are described in Appendix B.

Vent gas streams were analyzed using a Perkin-Elmer Sigma 3B gas chromatograph interfaced with a Perkin-Elmer Sigma 10 chromatography data station. Water collected in the high pressure knock-out vessel was analyzed for ammonia and sulphide using standard wet chemical methods.

The first liquefaction experiment, Run No. 9500, was made to condition the catalyst. The 24-hour run was conducted with Lingan Harbour seam coal at a slurry feedrate of 1.5 kg/hr and a total pressure of 17.24 MPa. First and second-stage reactor temperatures were 450 and 425°C respectively. A comparison of results from Run Nos. 9500 and 7007 are shown below. Run No. 7007 was the catalyst conditioning operation carried out earlier at thermal/catalytic processing conditions with Amocat 1C.

	Run No. 9500	Run No. 7007
Coal Conversion, Wt. %	93.4	91.5
Product Distribution, Wt. % maf Coal		
Gases	19.2	19.2
Oil	45.3	42.4
Asphaltenes	22.7	23.1
Preasphaltenes	6.2	6.8
Unreacted Coal	6.6	8.5
Hydrogen Consumption, Wt. % maf Coal	4.8	4.6

The results indicate that a slightly higher oil yield was achieved in Run No. 9500 with the Shell catalyst.

After completion of the catalyst conditioning operation a series of experiments were carried out varying coal feedstock and reactor temperature to further investigate the performance of Shell 317. A summary of the results from these experiments is shown in Table 16. Detailed performance and material balance data are presented in Appendices C and D.

Run Nos. 9501 and 9502 were conducted with Donkin Harbour seam coal. The temperature of the catalytic reactor in Run No. 9501 was 410°C. Coal conversion and

pentane soluble oil yield were 94 and 53% respectively. The reactor was operated at 425°C in Run No. 9502. The higher temperature caused an increase in gas production from 22 to 26% and raised the oil yield to 56%. Similar trends were observed in Run Nos. 9503 and 9505 with Prince Hub seam coal.

The three Sydney area coals and Illinois No. 6 were tested at similar operating conditions in Run Nos. 9504 - 9507 inclusive. The catalytic reactor was operated at 425°C in these runs. High coal conversion was achieved in all four experiments 94 - 97%. Product distribution varied considerably as a function of coal feedstock as illustrated in Figure 8. Gas yields ranged from 25% with Lingan Harbour seam coal to 31% with Illinois No. 6. Donkin Harbour, Prince Hub and Lingan Harbour seam coals produced 55, 54 and 50% oil respectively compared to 58% from Illinois No. 6. Lingan produced the highest yields of asphaltenes and preasphaltenes at 16 and 3%. The three Sydney area coals yielded higher levels of asphaltenic components than the American coal.

In all of the experiments except Run No. 9509 the concentration of coal in the feed slurry was fixed at 28 wt. %. In Run No. 9509 the coal loading was increased to 33 wt. %. A comparison of the results from Run Nos. 9504 and 9509 made with Donkin coal shows that the product distribution shifted downward slightly in the latter run. Furthermore, hydrogen consumption was measured at 8.7% in Run No. 9504 compared with 7.4% in Run No. 9509. Examination of the data presented in Table 17 shows that the higher coal loading in Run No. 9509 resulted in higher levels of nitrogen and sulphur in the product liquids.

TABLE 16

RESULTS FROM TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS WITH SHELL 317

RUN NO. COAL TESTED	9500 LINGAN HR-7	9501 DONKIN HR-10	9502 DONKIN HR-10	9503 PRINCE HB-9	9504 DONKIN HR-10
Temperatures: °C					
Thermal Dissolver	450	450	450	440	450
Catalytic Reactor	425	410	425	410	425
Back Pressure, MPa	17.24	19.30	19.30	19.30	19.30
Slurry Feedrate, kg/hr	1.503	1.022	1.017	0.998	0.997
H_2 Treatrate, Wt. % Dry Coal	10.0	20.6	20.7	21.1	21.2
Catalyst Age (kg coal/kg catalyst)	30	39	48	57	66
CONVERSIONS, WT. % OF maf COAL					
Pentane Solubles plus Gases	64.5	75.2	81.8	76.6	80.6
Toluene Solubles plus Gases	87.2	91.3	92.6	90.9	92.5
THF Solubles plus Gases	93.4	93.5	94.1	92.6	94.2
PRODUCT DISTRIBUTION, WT. % OF maf COAL					
Gases	19.2	22.4	25.8	23.6	26.0
Oil	45.3	52.8	56.0	53.0	54.6
Asphaltenes	22.7	16.1	10.8	14.3	11.9
Preasphaltenes	6.2	2.2	1.5	1.7	1.7
H_2 CONSUMPTION, WT. % OF maf COAL	4.8	7.7	9.0	7.9	8.7

TABLE 16 (continued)

RESULTS FROM TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS WITH SHELL 317

RUN NO. COAL TESTED	9505 PRINCE HB-9	9506 LINGAN HR-9	9507 ILLINOIS NO. 6	9508 PRINCE HB-9	9509 DONKIN HR-10
Temperatures: °C					
Thermal Dissolver	440	450	440	450	450
Catalytic Reactor	425	425	425	425	425
Back Pressure, MPa	19.30	19.30	19.30	19.30	19.30
Slurry Feedrate, kg/hr	1.022	0.998	1.015	1.015	1.032
H_2 Treatrate, Wt. % Dry Coal	20.6	21.1	20.6	20.8	20.4
Catalyst Age (kg coal/kg catalyst)	75	84	93	102	112
CONVERSIONS, WT. % OF maf COAL					
Pentane Solubles plus Gases	81.7	74.7	88.6	81.9	76.2
Toluene Solubles plus Gases	92.4	90.6	95.6	92.2	91.5
THF Solubles plus Gases	93.8	93.7	96.6	93.8	93.8
PRODUCT DISTRIBUTION, WT. % OF maf COAL					
Gases	27.7	25.0	31.0	29.7	24.4
Oil	54.0	49.7	57.6	52.2	51.8
Asphaltenes	10.7	15.9	6.9	10.3	15.3
Preasphaltenes	1.4	3.1	1.1	1.6	2.3
H_2 CONSUMPTION, WT. % OF maf COAL	7.4	7.4	8.4	7.7	7.4

Figure 8 - PRODUCT DISTRIBUTION AS A FUNCTION OF COAL FEEDSTOCK USING SHELL 317

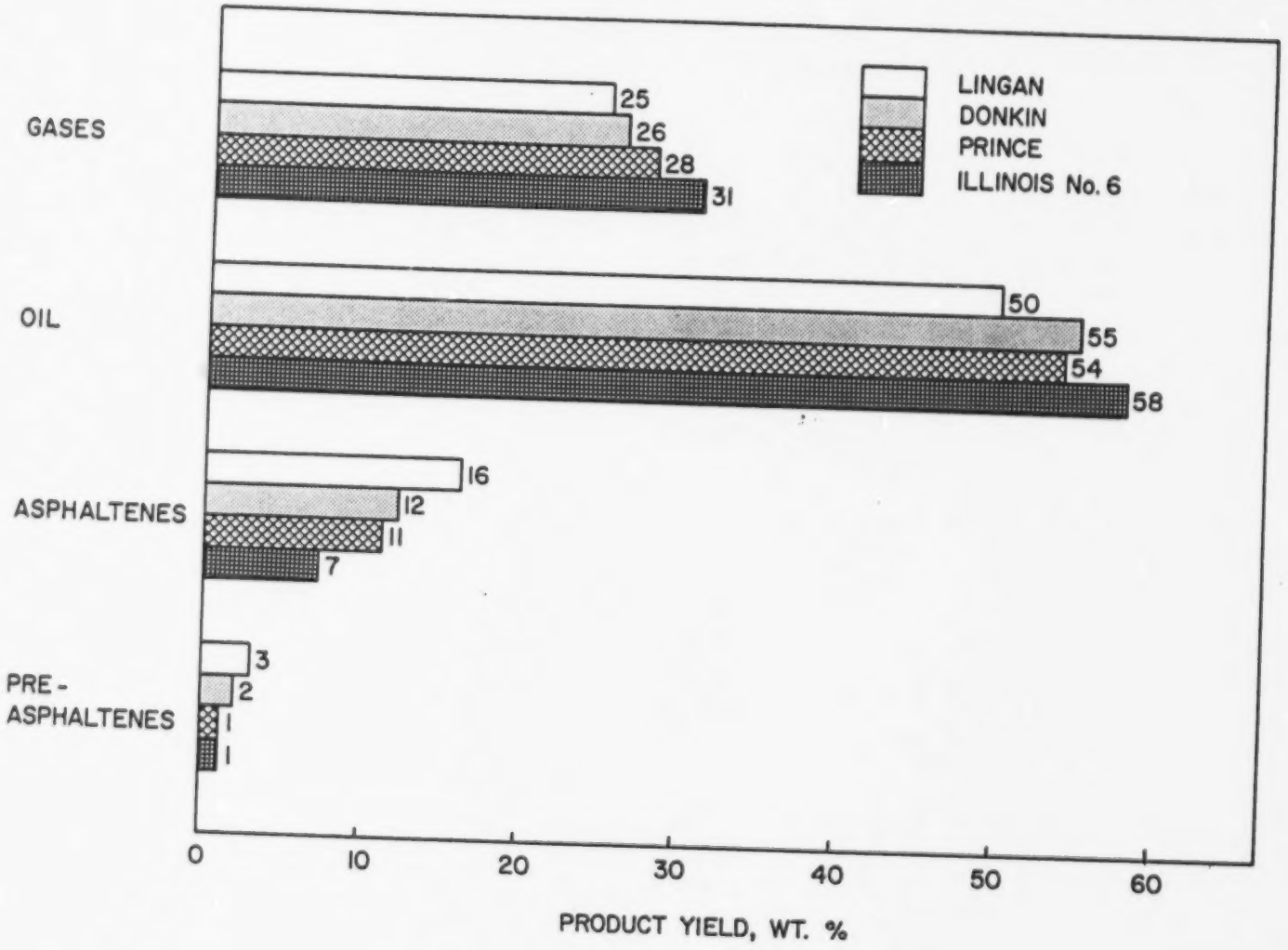


TABLE 17

ELEMENTAL ANALYSES ON PENTANE, TOLUENE AND THF SOLUBLE FRACTIONS
FROM TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO.	9500	9501	9502	9503	9504	9505	9506	9507	9508	9509
Pentane Soluble Fraction										
Carbon, Wt. %	90.66	89.31	89.91	89.77	89.52	90.22	90.52	89.80	90.45	90.44
Hydrogen, Wt. %	8.80	9.39	9.23	9.05	9.03	8.99	8.94	9.26	8.85	8.93
Nitrogen, Wt. %	0.29	0.23	0.22	0.23	0.23	0.20	0.26	0.21	0.20	0.22
Sulphur, Wt. %	0.023	0.026	0.024	0.030	0.026	0.030	0.027	0.031	0.032	0.035
Toluene Soluble Fraction										
Carbon, Wt. %	90.69	90.04	90.08	90.10	90.56	90.57	90.49	90.27	90.40	90.60
Hydrogen, Wt. %	8.53	8.97	8.99	8.84	8.87	8.84	8.63	8.89	8.69	8.70
Nitrogen, Wt. %	0.32	0.30	0.25	0.26	0.26	0.22	0.30	0.23	0.24	0.29
Sulphur, Wt. %	0.032	0.034	0.030	0.037	0.035	0.038	0.038	0.042	0.044	0.048
THF Soluble Fraction										
Carbon, Wt. %	89.71	89.63	89.37	90.11	90.19	90.06	90.34	89.82	90.36	89.76
Hydrogen, Wt. %	8.47	8.92	8.98	8.91	8.92	8.87	8.74	9.01	8.78	8.72
Nitrogen, Wt. %	0.44	0.32	0.28	0.28	0.26	0.25	0.34	0.32	0.30	0.33
Sulphur, Wt. %	0.038	0.041	0.037	0.042	0.042	0.045	0.045	0.056	0.049	0.054

6.3 Performance Comparison of Nickel-Molybdenum Bimodal Catalysts

The evaluation of hydroprocessing catalysts was an integral part of our program on advanced two-stage coal liquefaction. Recently, experimental work has been concentrated on evaluating the performance of nickel-molybdenum bimodal catalysts with Sydney area coals. Two commercial catalysts, Amocat 1C and Shell 317, have been tested rather extensively in thermal/catalytic operations. These catalysts differ moderately in metals loading, surface area and mean macropore diameter as shown in Table 1. Furthermore, Shell 317 is a trilobe shaped catalyst whereas Amocat 1C is a conventional cylindrical extrudate.

Coal conversion and raw product distribution were used as parameters in evaluating the performance of the catalysts. Direct comparisons were made between runs at similar operating conditions. Details pertaining to the runs with Amocat 1C are given in an earlier report (8).

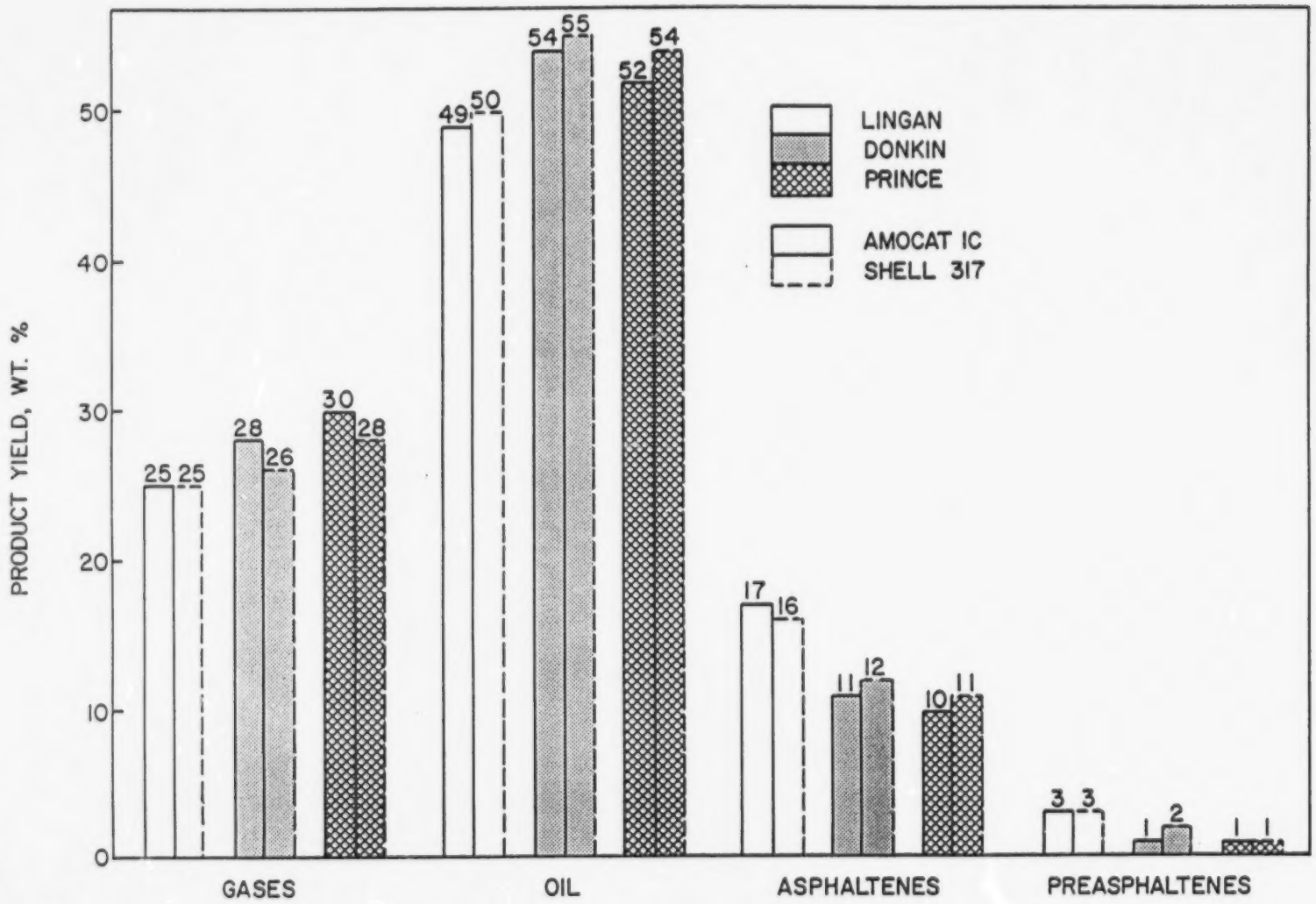
High coal conversion, 93 - 94%, was achieved with both catalysts at the operating conditions shown in Table 18. Product yields are illustrated for Lingan Harbour, Donkin Harbour and Prince Hub seam coals in Figure 9. Amocat 1C and Shell 317 produced similar product distributions with Donkin coal. This trend was also observed with the other coals. Hence the differences in metals loading, surface area and mean macropore diameter between the catalysts did not affect their relative performance significantly.

TABLE 18

COMPARISON OF TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION EXPERIMENTS WITH SHELL 317 AND AMOCAT 1C CATALYSTS

RUN NO. COAL TESTED CATALYST	9504 DONKIN SHELL 317	7014 DONKIN AMOCAT 1C	9505 PRINCE SHELL 317	7016 PRINCE AMOCAT 1C	9506 LINGAN SHELL 317	7015 LINGAN AMOCAT 1C
Temperatures: °C						
Thermal Dissolver	450	450	440	440	450	450
Catalytic Reactor	425	425	425	425	425	425
Back Pressure, MPa	19.30	20.68	19.30	20.68	19.30	20.68
Slurry Feedrate, kg/hr	0.997	0.982	1.022	1.007	0.998	1.007
H_2 Treatrate, Wt. % Dry Coal	21.2	25.5	20.6	24.8	21.1	24.8
Catalyst Age (kg coal/kg catalyst)	66	76	75	94	84	85
CONVERSIONS, WT. % OF maf COAL						
Pentane Solubles plus Gases	80.6	81.2	81.7	82.6	74.7	74.5
Toluene Solubles plus Gases	92.5	92.6	92.4	92.2	90.6	91.0
THF Solubles plus Gases	94.2	93.9	93.8	93.2	93.7	94.1
PRODUCT DISTRIBUTION, WT. % OF maf COAL						
Gases	26.0	27.7	27.7	30.2	25.0	25.2
Oil	54.6	53.5	54.0	52.4	49.7	49.3
Asphaltenes	11.9	11.4	10.7	9.6	15.9	16.5
Preasphaltenes	1.7	1.3	1.4	1.0	3.1	3.1
H_2 CONSUMPTION, WT. % OF maf COAL	8.7	8.3	7.4	7.1	7.4	6.6

Figure 9 - PRODUCT DISTRIBUTION FOR SYDNEY AREA COALS AS A FUNCTION OF CATALYST



CONCLUSIONS AND RECOMMENDATIONS

A research project on asphaltene conversion and catalyst regeneration in two-stage liquefaction of Nova Scotia coals has been completed. The project was aimed at improving distillate yield and reducing catalyst cost in two-stage operations. Laboratory experiments were carried out to screen potential asphaltene conversion catalysts and determine the degree to which the activity of aged coal liquefaction catalyst can be restored via controlled oxidation. In addition, a series of two-stage thermal/catalytic liquefaction bench runs were conducted with coals from the Sydney coalfield and Illinois No. 6 coal using Shell 317 catalyst.

A total of nine multi-functional catalysts designed for hydroprocessing heavy feeds were selected for the asphaltene conversion study. Alumina supported nickel-molybdenum, cobalt-molybdenum and nickel-tungsten type catalysts were tested. The alumina supports varied in shape, size, surface area, pore volume and modal pore size distribution. Coal liquefaction recycle liquid rich in asphaltenic material was used as feed.

Catalyst screening experiments were conducted in a high pressure batch reactor system at 425°C and 20.68 MPa for 60 minutes. Activity data were developed for pentane insolubles conversion (PIC), hydrogen content boost (HCB), hydrodenitrogenation (HDN) and hydrodesulphurization (HDS). PIC ranged from 35% with Katalco 550S to 45% with Shell 317. HCB ranged from 11% with Shell 324 to 15% with Shell 317. HDN ranged from 16% with Katalco 550S to 30% with Shell 317. HDS ranged from 58% with Shell 324 to 72% with Shell 317. In terms of overall performance, Shell 317 was found to be superior to the other catalysts tested.

The effect of residence time was investigated at 425°C and 20.68 MPa with Shell 317 nickel-molybdenum bimodal catalyst. Increasing the residence time from 30 to 90 minutes affected significant gains in PIC, HCB, HDN and HDS. Results were as follows:

- PIC increased from 39 to 51%
- HCB increased from 12 to 16%
- HDN increased from 19 to 33%
- HDS increased from 63 to 78%

Four aged Amocat 1C catalyst samples and one aged Katalco 550 sample were studied in the catalyst regeneration experiments. The samples were obtained from two-stage coal liquefaction bench unit operations at NSRFC. They ranged in age from 145 to 518 kg coal/kg catalyst. The samples were analyzed to determine both chemical and physical characteristics. Fresh, aged and regenerated samples were subjected to batch activity testing at the same operating conditions used for the catalyst screening experiments.

The results of the chemical analyses performed on fresh, used and regenerated samples show that all five used catalysts have substantial carbonaceous deposits, typically around 12 - 14%. Accumulations of iron, titanium and calcium on the samples were rather low. Iron accumulated to a greater extent than the other contaminant metals. The highest iron concentration, 1.07%, was measured on Amocat 1C at an age of 518 kg coal/kg catalyst.

The results of the physical characterization work show that the used catalysts have lower pore volumes and surface areas than fresh catalyst. However, these features were restored to a significant degree in the regenerated samples. For instance, Amocat 1C lost

34% of its original pore volume and 35% of its original surface area in a long-term recycle coal liquefaction run (RCL-9200) - after controlled carbon burnoff, the pore volume of the sample was 107% of the original whereas the surface area was 86%.

Results of the batch activity tests indicate that all five used catalysts experienced severe deactivation. Katalco 550, a unimodal mesopore catalyst, showed the greatest activity losses for all functionalities. Decreases in PIC, HCB, HDN and HDS ranged from 31 to 100%. Regeneration of the used catalyst resulted in significant restoration of all four activities. In fact, the activities were restored to levels ranging from 84 - 100% of their original values. Similar trends in activity losses and recoveries were measured for Amocat 1C.

A total of ten two-stage thermal/catalytic coal liquefaction experiments were carried out with Shell 317 nickel-molybdenum catalyst. Test work was concentrated on Harbour and Hub seam coals from the Sydney coalfield. One run was conducted with Illinois No. 6 coal for comparative purposes. The experiments were done in a once-through processing mode using hydrogenated anthracene oil containing 9% H as reaction solvent.

Experiments with Donkin Harbour coal showed that increasing the catalytic reactor temperature from 410 to 425°C had a positive effect on oil yield. Coal conversion was constant at 94%. Whereas, the higher temperature caused an increase in gas production from 22 to 26% and raised the oil yield from 53 to 56%. Similar trends were observed in runs with Prince Hub coal.

The three Sydney area coals and Illinois No. 6 were tested at similar operating conditions. The catalytic reactor temperature was 425°C in these tests. High coal conversion was achieved in all four experiments, 94 - 97%. Product distribution varied considerably as a function of coal feedstock. Gas yields ranged from 25% with Lingan Harbour coal to 31% with Illinois No. 6. Donkin Harbour, Prince Hub and Lingan Harbour coals produced 55, 54 and 50% oil respectively compared to 58% from Illinois No. 6.

Two nickel-molybdenum bimodal catalysts, Amocat 1C and Shell 317, have been tested in two-stage thermal/catalytic operations. These catalysts differ moderately in metals loading, pore volume, surface area and mean macropore diameter. A comparison of experimental results shows that the overall performance of Amocat 1C and Shell 317 are quite similar with the Sydney area coals at the operating conditions investigated.

Recommendations based on the findings of this project and other considerations are as follows:

(a) The need for basic research to develop better asphaltene conversion catalyst is evident. Therefore, it is recommended that efforts be undertaken to initiate collaborative programs on catalyst development involving government laboratories and interested private sector companies.

(b) The promising results achieved in the catalyst regeneration experiments suggest that further work in this area be pursued. Hence, it is

recommended that alternate heating methods for controlled carbon burnoff be investigated and that larger scale regeneration trials be undertaken.

(c) In order to assess the potential merits of advances in both new catalyst development and used catalyst regeneration, bench-scale coal liquefaction test work is recommended.

Opportunities exist in the area of catalysis applied to direct coal liquefaction. The use of a more active catalyst or the ability to extend catalyst service life would enhance the overall process and lower the cost of coal-derived liquids.

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APPENDIX A

DESCRIPTION OF TWO-STAGE COAL LIQUEFACTION BENCH UNIT

DESCRIPTION OF TWO-STAGE COAL LIQUEFACTION BENCH UNIT

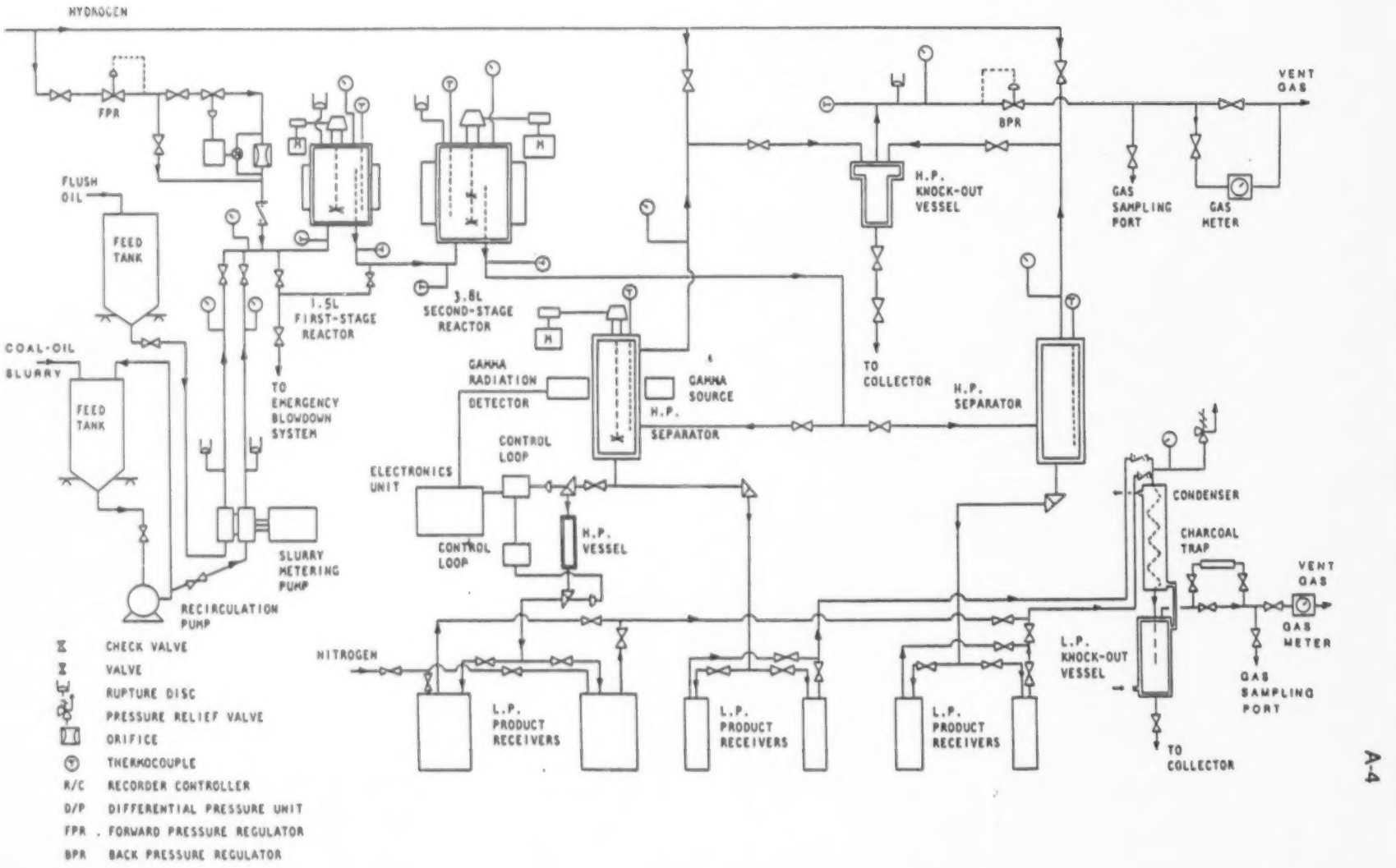
NSRFC's integrated two-stage coal liquefaction unit is designed for diverse applications. A schematic diagram of the system is shown in Figure 10. The design provides a closely coupled two-stage reaction zone and a separate feed circuit for flushing the unit. In this study, the unit was operated with a thermal first-stage and a catalytic second-stage. The apparatus is suitable for high pressure (24 MPa) use and is capable of processing 0.7 - 3.0 kg per hour of coal/oil slurry.

In the system, coal and oil are mixed batchwise in a 20-liter feed vessel. The coal/oil slurry is continuously circulated by a rotary pump. This arrangement prevents settling of coal fines and provides suction pressure to the slurry metering pump. Hydrogen is added and the mixture is fed to the 1.5-liter first-stage reactor. The reactor is heated by a two-zone electric heater. Effluent from the first-stage flows to the second-stage reactor. Downstream of the reaction zone, products are passed to a hot separator. The overhead vapours and gases from the hot separator pass to a cold knock-out vessel. Light liquid products are condensed in the cold knock-out and a vent gas stream is provided through a back pressure regulator. An automated high pressure let-down system controls the rate at which slurry product is withdrawn from the bottom of the hot separator. The bottoms slurry is flashed at atmospheric pressure and collected. Vapours and gases from the low pressure product receivers are passed through a water-cooled knock-out vessel and condenser. Vent gas streams are monitored with gas meters.

The 3.8-liter second-stage reactor is a stirred tank reactor modified to function in a catalytic mode. This was accomplished by installing a catalyst basket assembly and an impeller/baffle system in the reactor. The capacity of the catalyst basket is about 600 cc. The components required were manufactured by Autoclave Engineers Inc. and are commonly known as Robinson-Mahoney style internals.

During operation, hot reacting slurry is constantly recirculated within the gradientless catalytic reactor. Slurry is forced through the annular basket and consequently across the catalyst by the impeller situated in the open area in the center of the basket. Slurry product and gases exit the reactor via an overflow pipe. This configuration permits catalyst to be used in bead or extrudate form. Furthermore, catalyst can be sulphided in-situ prior to coal liquefaction runs.

Figure 10 - SCHEMATIC DIAGRAM OF TWO-STAGE COAL LIQUEFACTION BENCH UNIT



APPENDIX B

CONVERSION CALCULATIONS

CONVERSION CALCULATIONS FOR CONTINUOUS COAL LIQUEFACTION EXPERIMENTS

Calculations are based on operations during the steady state sampling period.

CONVERSIONS, WT. %:

$$\text{Pentane sol. + gases} = \frac{\text{(maf coal charged) - (organic pentane insol.)}}{\text{maf coal charged}} \times 100$$

$$\text{Toluene sol. + gases} = \frac{\text{(maf coal charged) - (organic toluene insol.)}}{\text{maf coal charged}} \times 100$$

$$\text{THF sol. + gases} = \frac{\text{(maf coal charged) - (organic THF insol.)}}{\text{maf coal charged}} \times 100$$

$$\text{Gases} = \frac{\text{product gases}}{\text{maf coal charged}} \times 100$$

DEFINITION OF PRODUCTS

Oil = pentane solubles

Asphaltenes = toluene solubles - pentane solubles

Preasphaltenes = THF solubles - toluene solubles

APPENDIX C

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO. COAL TESTED CATALYST	9500 LINGAN HR-7 SHELL 317	9501 DONKIN HR-10 SHELL 317	9502 DONKIN HR-10 SHELL 317	9503 PRINCE HB-9 SHELL 317
A. OPERATING CONDITIONS				
Unit back pressure, MPa	17.24	19.30	19.30	19.30
Temperatures, °C:				
Thermal Dissolver	450	450	450	440
Catalytic Reactor	425	410	425	410
Slurry Preheater	250	250	250	250
Hot Separator	300	300	300	300
Feedrates:				
Slurry, kg/hr	1.503	1.022	1.017	0.998
Raw Coal, kg/hr	0.421	0.286	0.285	0.279
Hydrogen, L/hr	462	642	642	636
SHSV, hr^{-1}; Thermal Dissolver	1.50	1.00	1.00	1.00
Catalytic Reactor	0.50	0.33	0.33	0.33
Hydrogen Treatrate, Wt. % Dry Coal	10.0	20.6	20.7	21.1
Catalyst Age (kg coal/kg catalyst)	30	39	48	57
B. CONVERSIONS OF maf COAL, WT. %				
Pentane Solubles plus Gases	64.5	75.2	81.8	76.6
Toluene Solubles plus Gases	87.2	91.3	92.6	90.9
THF Solubles plus Gases	93.4	93.5	94.1	92.6
C. PRODUCT YIELDS ON maf COAL, WT. %				
CH_4	3.6	3.7	4.3	2.8
C_2H_6	2.9	3.3	4.2	3.0
C_3H_8	2.3	2.7	3.7	2.5
C_4H_{10}	2.2	3.0	3.5	2.9
CO	0.1	0.2	0.0	0.2
H_2S	0.8	1.4	1.4	1.9
H_2O	6.6	7.1	7.6	9.3
NH_3	0.7	1.0	1.1	1.0
Oil	45.3	52.8	56.0	53.0
Asphaltenes	22.7	16.1	10.8	14.3
Preasphaltenes	6.2	2.2	1.5	1.7
Unreacted Coal	6.6	6.5	5.9	7.4
D. H_2 CONSUMPTION, WT. % OF maf COAL	4.8	7.7	9.0	7.9

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO. COAL TESTED CATALYST	9504 DONKIN HR-10 SHELL 317	9505 PRINCE HB-9 SHELL 317	9506 LINGAN HR-9 SHELL 317	9507 ILLINOIS NO. 6 SHELL 317
A. OPERATING CONDITIONS				
Unit back pressure, MPa	19.30	19.30	19.30	19.30
Temperatures, °C:				
Thermal Dissolver	450	440	450	440
Catalytic Reactor	425	425	425	425
Slurry Preheater	250	250	250	250
Hot Separator	300	300	300	300
Feedrates:				
Slurry, kg/hr	0.997	1.022	0.998	1.015
Raw Coal, kg/hr	0.279	0.286	0.279	0.284
Hydrogen, L/hr	642	636	648	630
SHSV, hr^{-1}; Thermal Dissolver	1.00	1.00	1.00	1.00
Catalytic Reactor	0.33	0.33	0.33	0.33
Hydrogen Treatrate, Wt. % Dry Coal	21.2	20.6	21.1	20.6
Catalyst Age (kg coal/kg catalyst)	66	75	84	93
B. CONVERSIONS OF maf COAL, WT. %				
Pentane Solubles plus Gases	80.6	81.7	74.7	88.6
Toluene Solubles plus Gases	92.5	92.4	90.6	95.5
THF Solubles plus Gases	94.2	93.8	93.7	96.6
C. PRODUCT YIELDS ON maf COAL, WT. %				
CH_4	4.1	3.6	4.4	3.5
C_2H_6	4.1	3.8	4.2	3.8
C_3H_8	3.7	3.5	3.8	3.6
C_4H_{10}	4.1	3.9	4.1	4.0
CO	0.1	0.2	0.2	0.3
H_2S	1.5	2.0	1.2	2.4
H_2O	7.3	9.6	6.1	12.2
NH_3	1.1	1.1	1.0	1.2
Oil	54.6	54.0	49.7	57.6
Asphaltenes	11.9	10.7	15.9	6.9
Preasphaltenes	1.7	1.4	3.1	1.1
Unreacted Coal	5.8	6.2	6.3	3.4
D. H_2 CONSUMPTION, WT. % OF maf COAL	8.7	7.4	7.4	8.4

SUMMARY OF OPERATING CONDITIONS AND PERFORMANCE FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO.	9508	9509
COAL TESTED	PRINCE HB-9	DONKIN HR-10
CATALYST	SHELL 317	SHELL 317
A. OPERATING CONDITIONS		
Unit back pressure, MPa	19.30	19.30
Temperatures, °C:		
Thermal Dissolver	450	450
Catalytic Reactor	425	425
Slurry Preheater	250	250
Hot Separator	300	300
Feedrates:		
Slurry, kg/hr	1.015	1.032
Raw Coal, kg/hr	0.284	0.341
Hydrogen, L/hr	636	756
SHSV, hr^{-1}; Thermal Dissolver	1.00	1.00
Catalytic Reactor	0.33	0.33
Hydrogen Treatrate, Wt. % Dry Coal	20.8	20.4
Catalyst Age (kg coal/kg catalyst)	102	112
B. CONVERSIONS OF maf COAL, WT. %		
Pentane Solubles plus Gases	81.9	76.2
Toluene Solubles plus Gases	92.2	91.5
THF Solubles plus Gases	93.8	93.8
C. PRODUCT YIELDS ON maf COAL, WT. %		
CH_4	4.3	4.1
C_2H_6	4.5	3.9
C_3H_8	4.2	3.4
C_4H_{10}	3.7	3.3
CO	0.3	0.2
H_2S	2.1	1.5
H_2O	9.5	7.1
NH_3	1.1	0.9
Oil	52.2	51.8
Asphaltenes	10.3	15.3
Preasphaltenes	1.6	2.3
Unreacted Coal	6.2	6.2
D. H_2 CONSUMPTION, WT. % OF maf COAL	7.7	7.4

APPENDIX D

MATERIAL BALANCES FOR TWO STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

MATERIAL BALANCES FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO.	9500	9501	9502	9503
COAL TESTED	LINGAN HR-7	DONKIN HR-10	DONKIN HR-10	PRINCE HB-9
CATALYST	SHELL 317	SHELL 317	SHELL 317	SHELL 317
MOISTURE, WT. %	1.15	2.14	2.14	2.91
ASH, WT. % DRY BASIS	3.42	6.01	6.01	7.20
HOURS ON STREAM	24.08	10.05	10.01	10.07
DURATION OF BALANCE PERIOD, HRS.	6.00	2.00	2.01	2.04
INPUT (g):				
H_2O	29.0	12.2	12.3	16.6
Ash	85.3	33.7	33.7	39.8
maf Coal	2410	526	527	513
Solvent	6491	1472	1472	1465
H_2	249.5	115.6	116.1	116.8
Total	9265	2160	2161	2151
OUTPUT (g):				
H_2O	187.2	49.8	52.3	64.2
Ash	82.2	30.2	26.9	38.6
Organic THF Insolubles[1]	159.2	34.4	31.2	37.8
THF Solubles[2]	8348	1879	1822	1882
H_2	133.2	75.1	68.7	76.3
Other Gases	305.1	80.6	95.6	73.7
Total	9215	2149	2097	2173
TOTAL MATERIAL RECOVERY, WT. %	99.5	99.5	97.0	101.0

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

MATERIAL BALANCES FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO.	9504	9505	9506	9507
COAL TESTED	DONKIN HR-10	PRINCE HB-9	LINGAN HR-9	ILLINOIS NO. 6
CATALYST	SHELL 317	SHELL 317	SHELL 317	SHELL 317
MOISTURE, WT. %	2.14	2.91	0.95	3.23
ASH, WT. % DRY BASIS	6.01	7.20	4.18	9.75
HOURS ON STREAM	10.04	10.02	10.01	10.03
DURATION OF BALANCE PERIOD, HRS.	2.03	2.02	2.01	2.02
INPUT (g):				
H_2O	12.1	16.8	5.3	18.5
Ash	33.3	40.4	23.2	54.2
maf Coal	521	521	533	501
Solvent	1457	1487	1444	1476
H_2	117.3	115.6	117.2	114.5
Total	2141	2181	2123	2164
OUTPUT (g):				
H_2O	50.0	66.9	37.8	79.7
Ash	26.0	31.3	18.2	37.6
Organic THF Insolubles[1]	30.4	32.2	33.7	16.9
THF Solubles[2]	1849	1843	1814	1837
H_2	72.0	77.0	77.8	72.4
Other Gases	98.1	94.0	100.8	93.5
Total	2126	2144	2082	2137
TOTAL MATERIAL RECOVERY, WT. %	99.3	98.3	98.1	98.8

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes

MATERIAL BALANCES FOR TWO-STAGE THERMAL/CATALYTIC LIQUEFACTION TESTS

RUN NO.	9508	9509
COAL TESTED	PRINCE HB-9	DONKIN HR-10
CATALYST	SHELL 317	SHELL 317
MOISTURE, WT. %	2.91	2.14
ASH, WT. % DRY BASIS	7.20	6.01
HOURS ON STREAM	10.00	10.03
DURATION OF BALANCE PERIOD, HRS.	2.01	2.05
INPUT (g):		
H_2O	16.6	14.9
Ash	39.9	41.0
maf Coal	515	642
Solvent	1469	1417
H_2	115.1	139.5
Total	2156	2254
OUTPUT (g):		
H_2O	65.5	60.8
Ash	31.8	33.1
Organic THF Insolubles[1]	32.0	39.7
THF Solubles[2]	1805	1866
H_2	75.4	92.0
Other Gases	103.9	111.6
Total	2114	2203
TOTAL MATERIAL RECOVERY, WT. %	98.1	97.7

1 - Unreacted coal
2 - Oil, asphaltenes and preasphaltenes